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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

4628. **Ion-exchange resins as reaction media for micro-detection tests.** Masatoshi Fujimoto (Dept. of Chem., Fac. of Sci., Univ. of Tokyo, Japan). *Chemist Analyst*, 1960, **49** (1), 4–10.—Detailed descriptions of resin spot-tests for 14 ions are given, together with identification and dilution limits. (52 references.) G. S. ROBERTS

4629. **Zinc acetate as a reagent in gravimetric analysis. I.** I. K. Taimni and Manohar Lal (Univ. of Allahabad, India). *Anal. Chim. Acta*, 1960, **22** (3), 236–238 (in English).—Iodide can be quant. separated from arsenate, phosphite, selenite, tellurite or tellurate by adding Na_2CO_3 and an excess of Zn acetate, boiling and filtering. Iodide is then determined in the filtrate, either gravimetrically as AgI or volumetrically with eosin as adsorption indicator, with an accuracy of $\pm 0{\cdot}3\%$. Rhenium can also be separated from arsenate, tellurate and tellurite by the same procedure and determined as the sulphide with an accuracy of $\simeq \pm 0{\cdot}4\%$. W. T. CARTER

4630. **Modified aluminon reagent solution.** A. G. Owen and W. J. Price (Chem. Res. Dept., Magnesium Elektron Ltd., Manchester, England). *Analyst*, 1960, **85**, 221–222.—Glacial acetic acid (80 ml), a soln. of 1 g of aluminon in 100 ml of water and a soln. of 2 g of benzoic acid in 300 ml of *iso*propyl alcohol are added to a soln. of 500 g of ammonium acetate in 1 litre of water. *iso*Propyl alcohol (450 ml) is added to the mixture, which is then diluted with water to 2 litres. This soln. is gradually added to a filtered 1% soln. of gelatin in water. When stored in polyethylene bottles in the dark, the reagent is stable for at least a month. Quoted results with known amounts of Al indicate a high degree of reproducibility. A. O. JONES

4631. **Analytical aspects of some azo dyes from chromotropic acid. X. Analytical reactions of some dyes from sulphonamides.** Sachindra Kumar Datta and Sachindra Nath Saha [Victoria (Government) College, Coochbehar, India]. *Z. anal. Chem.*, 1960, **174** (1), 38–44 (in English).—Six azo compounds have been prepared by diazotising sulphanilamide, sulphapyridine, sulphadiazine, sulphaguanidine, sulphamerazine and sulphathiazole and coupling the products with chromotropic acid. The products give colour reactions with Co^{2+}, Ni^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Be^{2+}, Al^{3+}, Fe^{3+}, Th^{4+}, Zr^{4+}, La^{3+}, Ce^{3+} and Ce^{4+}, and are of particular value as sensitive reagents for Th^{IV} at pH 3 (as little as 1·2 μg may be detected by spot-test technique on paper). The compounds prepared from sulphadiazine and sulphamerazine also react with Li^+ at pH 8 to give a pink colour. T. R. ANDREW

4632. **Pyromellitein indicators. II. Adsorption indicators.** J. A. Bishop (Coll. of Engng, Newark, N.J., U.S.A.). *Anal. Chim. Acta*, 1960, **22** (3), 221–222 (in English).—Tetraresorcinol pyromellitein (**I**) and diresorcinol diphenol pyromellitein (**II**) can be used as adsorption indicators for the argentimetric titration of halides and thiocyanate. **I** can be used in place of dichlorofluorescein (**III**) for the titration of halides. **II** gives poor results for Cl^- in neutral or slightly acid soln., but good ones in more acid soln. (where **III** cannot be used) even in the presence of coloured ions, *e.g.*, Cr^{3+}, Fe^{3+}, Cu^{2+}, Ni^{2+} and Co^{2+}. **II** is excellent for the titration of Br^-, I^- and SCN^-, and better than **I** for the titration of very dilute soln. of all three halides in weak acid soln. W. T. CARTER

4633. **NNN′N′-Tetracarboxymethyl derivatives of some benzidines as metallofluorescent indicators.** R. Belcher, D. I. Rees and W. I. Stephen (Univ., Birmingham, England). *Talanta*, 1960, **4** (1), 78–79.—Of 3 new EDTA analogues derived from 3:3′-disubstituted benzidine, *viz*, *o*-dianisidine- (**I**), *o*-diphenetidine- (**II**), and 3:3′-dicarboxybenzidine-NNN′N′-tetra-acetic acid (**III**), **I** and **II** fluoresce intensely in soln. between pH 4 and 10 (optimally at pH 5·5 to 6) and **III** at pH > 8 (optimally in NaOH soln.). Fluorescence of **I** and **II** is quenched by Cu^{II} and Hg^{II} and of **III** by Ca; 0·035 μg of Cu is detectable at a dilution of 0·5 p.p.m. The sodium salts are used as indicators in EDTA titrations. J. P. STERN

4634. **Umbellicomplexone and xanthocomplexone—complexometric fluorescent indicators.** J. H. Eggers (Swedish Wood Research Inst., Stockholm). *Talanta*, 1960, **4** (1), 38–43 (in German).—Condensation of formaldehyde and iminodiacetic acid with 4-methylumbelliferone and 3:6-dihydroxyxanthone affords, respectively, umbellicomplexone (**I**) and xanthocomplexone (**II**) which form fluorescent complexes at pH > 9 with cations with complete electron shells, *e.g.*, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Zn^{2+} and Cd^{2+}. Thus **I** and **II** are useful as indicators in complexometry. Free **I** and **II** lose their fluorescence above pH 12, but interfering background fluorescence at high pH, due to high concn. of Na^+, can be reduced by warming the soln. J. P. STERN

4635. **Standardisation of mercury(II) chloride solution.** G. Matsuyama (Union Oil Co. of California, Brea, U.S.A.). *Chemist Analyst*, 1960, **19** (1), 21.—The H^+ liberated when H_2S is passed through $HgCl_2$ soln. are titrated with standard alkali soln. to a methyl purple end-point. G. S. ROBERTS

4636. **Some theoretical considerations in analytical chemistry. V. A simple method of calculating acid - base titration errors.** E. Bishop (Washington Singer Lab., Univ. Exeter, England). *Anal. Chim. Acta*, 1960, **22** (3), 205–213 (in English).—The error in acid - base titrations can be subdivided into a

chemical error due to disparity between the end- and equivalence-points, a visual discrimination error in detecting the colour change of the indicator and an error due to consumption of titrant by the indicator. Normally only the first of these is significant and expressions for it are derived which take into account the strengths of the acid and base, the hydrolysis of the salt produced in the titration and the ionisation of the solvent.

W. T. CARTER

4637. **Micro-determinations in non-aqueous media.** L. Serrano Berges (Univ. of Birmingham, England). *Inf. Quim. Anal.*, 1960, **14** (2), 41–50.—For the titration of bases, the sample (300 to 500 μg) is dissolved in glacial acetic acid and either titrated directly with 0·02 *N* $HClO_4$ in acetic acid, or treated with an excess of this soln. and back-titrated with 0·02 *N* Na acetate in acetic acid, with crystal violet as indicator. The method has been used for sodium salts of org. acids and amino acids, with an accuracy of $\pm 1\%$, and for quaternary ammonium halides with an accuracy of $\pm 2\%$. L. A. O'NEILL

4638. **Osmium tetroxide as general catalyst for oxidations in alkaline media.** F. Solymosi and J. Csik (Inst. of Inorg. and Anal. Chem., Univ. of Szeged, Hungary). *Chemist Analyst*, 1960, **49** (1), 12–13.—Oxidations with alkaline ferricyanide catalysed by osmium tetroxide may be used in the titrimetric determination of thiocyanate, thiosulphate, selenite, arsenite, sulphite, tetrathionate and ferricyanide itself. Osmium tetroxide also has a catalytic influence on the oxidation reactions in alkaline media of hypochlorite, hypobromite, hypoiodite, permanganate and chloramine T.

G. S. ROBERTS

4639. **Mechanism of oxidation by cerate - chromate reagent.** N. N. Sharma and R. C. Mehrotra (Chem. Lab., Univ. of Allahabad and Gorakhpur, India). *Z. anal. Chem.*, 1960, **173** (5), 395–399 (in English).—The kinetics of the reaction between formic acid and $Ce(SO_4)_2$ in the presence of Cr and H_2SO_4 (*cf.* Sharma, *Anal. Abstr.*, 1957, **4**, 2234; 1958, **5**, 561; 1959, **6**, 1787) have been studied. The reaction is of the first order with respect to formic acid and the unimolecular constant is proportional to the concn. of chromium ions; the rate constant is proportional to the square of the H_2SO_4 concn. but is independent of the valency state of the chromium ions initially present, provided that their molar concn. remains the same. If Cr^{3+} are present these are oxidised by $Ce(SO_4)_2$ to Cr^{6+} which then oxidise the organic compound. The reagent is a more powerful oxidising agent than chromate alone, particularly when the oxidation is not controlled by redox potential alone. It is also more stable at higher temp. P. D. PARR-RICHARD

4640. **Coulometric titrations with electrolytically generated sulphydryl [mercapto] compounds. Applications of thioglycollic acid.** B. Miller and D. N. Hume (Dept. of Chem., M.I.T., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 524–528.—The mercapto group forms complexes with metals such as Cu, Au and Hg and with ferricyanide, and their coulometric determination has been investigated. In the procedure described, the reagent is generated from thioglycollic acid, and a mercury pM electrode is used for end-point detection. Amperometry at two mercury electrodes is also feasible.

K. A. PROCTOR

4641. **Further possibilities in flame photometry.** K. Konopicky and W. Schmidt (Forschungsinst. d. Feuerfest Ind., Bonn, Germany). *Z. anal. Chem.*, 1960, **173** (5) 358–369.—The addition of *n*-butanol is known to increase the emission of Al at 484 mμ. In the present study, the spectra of elements such as Fe and B, in H_2O and in 4% *n*-butanol, are compared with the background emission given by H_2O or 4% *n*-butanol alone. The total intensity of a band or line is composed of different factors. The effective intensity is given by the increase due to *n*-butanol. The influence of gas pressure on intensity is discussed. Advantages of adding *n*-butanol include the intensification of weak bands or lines which may occur at wavelengths where interference is least, and the greater intensification of bands relative to lines, so that the effect of interfering lines may be lessened. Examples are given and the mutual influence of various ions present in silicates is discussed.

P. D. PARR-RICHARD

4642. **Analytical applications of the measurement of ionisation constants.** P. Rumpf (Centre d'Étud. et de Recherches de Chim. Organ. Appliqué, C.N.R.S., Bellevue, S. et O., France). *Chim. Anal.*, 1960, **42** (3), 111–116.—The relation between structure of organic acids and their acidity is discussed. Attention is drawn to the use of ionisation constants in the detection of certain functional groups and structures. J. H. WATON

See also Abstracts—**4675**, Metallochromic indicator for Ca. **4679**, Use of unithiol for Zn. **4715**, Thiomalic acid as reagent for Zr. **4764**, Use of 3-acetyl-4-hydroxycoumarin. **4796**, NN′-Bis-(3-dimethylaminopropyl)dithio-oxamide as reagent for Pd.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

4643. **Symposium on solvent extraction in the analysis of metals.** *A.S.T.M. Spec. Tech. Publ.*, 1959, No. 238, 54 pp.—**Introduction,** H. Freiser and G. H. Morrison, pp. 1–4. **Convergence of tie lines in ternary liquid systems and its application to liquid extraction,** R. L. Pilloton, pp. 5–12. **Metals analysis with thenoyltrifluoroacetone,** F. L. Moore, pp. 13–26. **Use of trioctylphosphine oxide in analytical chemistry,** J. C. White, pp. 27–35. **8-Hydroxyquinaldine extraction applied to the analysis of metals,** R. J. Hynek, pp. 36–42. **Use of organic solvents in flame photometry,** J. A. Dean, pp. 43–54. J. IRON ST. INST. ABSTR.

4644. **Determination of small stoicheiometric deviations in oxide monocrystals.** H. B. Sachse (Keystone Carbon Co., St. Marys, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 529–530.—The oxygen surplus in monocrystals of manganous, cobaltous and nickelous oxides was determined by a modified Bunsen method, which allows the measurement of deviations down to one milli-atom of oxygen per mol. of monoxide with an accuracy of the order of $\pm 10\%$. The detection of smaller deviations is possible, but with an increased error.

K. A. PROCTOR

4645. **Determination and reactions of some acidic oxy-anions in fused chlorides and nitrates.** J. D. Van Norman and R. A. Osteryoung (Dept. of Chem.,

Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 398–400.—Acid oxy-anions such as $Cr_2O_7^{2-}$, PO_3^- and VO_3^- may be determined in a LiCl - KCl melt by adding an excess of Na_2CO_3 and measuring the CO_2 evolved. A similar reaction occurs in a $NaNO_3$ - KNO_3 melt with $Cr_2O_7^{2-}$, but not with PO_4^- or $S_2O_7^{2-}$. It should be possible to determine an oxide ion by adding a known excess of an acidic oxy-anion and titrating the unchanged acid with carbonate.

J. H. WATON

4646. **Separation of various anions by paper chromatography.** H. Laub (Lab. Siemens-Schuckertwerke A.-G., Nürnberg, Germany). *Z. anal. Chem.*, 1960, **173** (3), 208–210 (in German).—The following anions show good separation by ascending paper chromatography (8 hr.) with the solvent butanol - acetone - water (5:2:3)—ClO_4^-, ClO_3^-, ClO_2^-, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, BrO_3^- and IO_3^-. About 30 μg of substance is used and spots are applied 30 mm apart. The procedures for colour development are as follows—ClO_2^-, spray with 0·2% KI soln. in 2 *N* HCl—brown spots; ClO_3^-, spray with KI in 2 *N* HCl, warm in hot air—brown spots; ClO_4^-, spray with saturated Na acetate soln., dry and spray with 0·5% aq. methylene blue—purple spots; Cl^-, Br^- and I^-, immerse in 2 *N* $AgNO_3$, wash with water and dry—I^- appear immediately, Br^- and Cl^- after drying, as violet spots (more rapidly under a quartz lamp) [alternatively, $(NH_4)_2S$ soln. may be applied by spraying after drying]; BrO_3^-, IO_3^-, NO_3^-, spray with 0·2% KI soln. in 2 *N* HCl; NO_3^-, diphenylamine in conc. H_2SO_4 is applied along a line and the excess is washed out immediately with water—blue spots become green after being washed. The R_F value is measured immediately on removal of the chromatogram from the tank.

P. G.

4647. **Spectrophotometric stability of metal oxinates on filter-paper.** A. Lacourt and P. Heyndryckx (Univ., Brussels). *Mikrochim. Acta*, 1960, (3), 473–474 (in English).—The stability of the oxinates of Co, Cu, Zn, Cd, Pb and Ba on filter-paper has been examined with respect to their extinctions at 360 mμ. With the exception of Pb the reproducibility is good up to at least 45 min. after spraying. Reproducible results are obtained with the lead compound up to 30 min. after spraying.

T. R. ANDREW

4648. **Adsorption of the elements from hydrofluoric acid by anion exchange.** J. P. Faris (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 520–522.—The elution characteristics for 48 elements are reported for Dowex 1-X10 anion-exchange resin (F^- form) and HF concn. from 1*M* to 24 *M*. The possibility of using the technique to separate binary mixtures may be assessed from the values presented.

T. R. ANDREW

4649. **Analytical applications of complexones. XXVI. Application of AEGT and ADCT to the volumetric micro-determination of the sum of metal cations.** F. Bermejo Martínez, M. Paz Castro and R. Rey Mendoza (Univ. of Santiago de Compostela, Spain). *Inf. Quím. Anal.*, 1960, **14** (2), 34–37.—Metal cations are determined by treatment with AEGT [1:2-di-(2-aminoethoxy)ethane-NNN′N′-tetra-acetic acid] (**I**) and ADCT (1:2-diamino*cyclo*hexane-NNN′N′-tetra-acetic acid) (**II**) at pH 11 to 12, followed by back-titration with standard aq. $CaCl_2$ soln., with murexide as indicator. Under these conditions **I** gives the sum of Cu and Zn, and **II** gives the sum of Fe, Al, Cu and Zn.

L. A. O'NEILL

4650. **Photochemical determination of metal cations by means of ethylenediaminetetra-acetic acid.** J. Joussot-Dubien and G. Oster (Lab. de Chim. Phys., Fac des Sci., Bordeaux, France). *Bull. Soc. Chim. France*, 1960, (2), 343–345.—Thiazine dyes such as methylene blue and thionine are photochemically reduced by free EDTA with a quantum efficiency of $\simeq$0·2, but not by metal - EDTA complexes. The max. rate of photo-reduction of thionine occurs at pH 6 and of methylene blue at pH 10 to 11. Those metal cations which are held in ammoniacal soln. at pH 10 to 11 (Ca^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) can be titrated directly with EDTA in an inert atmosphere, with strongly illuminated methylene blue as indicator. Cations normally determined by back-titration of excess of EDTA with $Mg(NO_3)_2$ (Pb^{2+}, Hg^{2+}, Al^{3+} and Fe^{3+}) can be titrated directly at pH 6 by the use of thionine. Oxygen rapidly oxidises the leuco base formed and must be excluded. *Procedure*—A measured soln. containing the cation ($\leqslant 10^{-4}M$), a buffer soln. (acetate for acid, phosphate for neutral and NH_4Cl - aq. NH_3 for alkaline soln.) and a few drops of the dyestuff ($\simeq 10^{-5}M$) are placed in a cell provided with a nitrogen bubbler. EDTA (disodium salt) soln. is added dropwise (5 to 6 drops per sec. at the end-point) and the soln. is strongly illuminated by means of a projector with a 300 to 500-W tungsten lamp. Although the colour becomes paler throughout the titration, in the strong light the eye only appreciates the sudden discharge of colour at the end-point. The Hg^{2+} titration has to be carried out at 60°, as the EDTA reacts too slowly with the cation at room temp.

E. J. H. BIRCH

4651. **Radiometric micro-method for the quantitative determination of metal ions.** E. Schumacher and W. Friedli (Anorg.-chem. Inst., Univ., Zurich). *Helv. Chim. Acta*, 1960, **43** (4), 1013–1018 (in German).—The difference in behaviour, as regards chromatography and ion exchange, of metal ions and their EDTA chelates is used for the determination of small amounts ($\simeq$0·01 μg) of metals. To the sample is added a known small quantity of a radioactive isotope of the metal sought and a known amount of EDTA (disodium salt), insufficient to react with all the metal ion present. The metal ions and the metal - EDTA chelate are separated by paper chromatography or ion exchange and their relative activities are determined. From the results the amount of metal ion originally present may be calculated. Examples are given of the application of the technique to determinations of Co and Tb.

T. R. ANDREW

4652. **Pre-oxidation by iodine chloride - potassium hydroxide, and use of iodine chloride end-point in the determination of hydrazine, thiocyanate, thiosulphate and glucose.** B. Sharma (Hindu Univ., Benares, India). *Bull. Chem. Soc. Japan*, 1960, **33** (3), 279–282 (in English).—Hydrazine sulphate ($\simeq$0·1 *N*), SCN^- and $S_2O_3^{2-}$ ($\simeq$0·01 *M*) can be determined accurately by pre-oxidation with hypoiodite at 25° followed by back-titration. A 50% excess of 0·5 *M* iodine chloride is added to the sample soln. (10 to 20 ml) followed by 25% aq. KOH soln. until the normality is between 1 and 2 (for soln. containing $S_2O_3^{2-}$ the alkali is added

before the iodine chloride). After ≃5 to 10 min., the mixture is adjusted to between 5 and 6 *N* in HCl and is then titrated amperometrically with 0·1 *N* KIO_3, $KMnO_4$ or $Ce(SO_4)_2$, the end-point being detected by the dead-stop method. The procedure is also applicable to the determination of glucose (≃1% concn.) provided that only just sufficient KOH to dissolve the liberated iodine is first added to the mixture of glucose and iodine chloride, followed by a little more alkali to convert iodine into hypoiodite. W. J. BAKER

4653. **Analytical aspects of some organic acids. V. Back-titration procedures for the determination of aluminium, zirconium and thorium with iron(III) solution and 3-hydroxy-2-naphthoic acid as indicator.** C. S. Pande and T. S. Srivastava (Chem. Dept., Lucknow Univ., India). *Z. anal. Chem.*, 1960, **173** (3), 195–198 (in English).—EDTA (disodium salt) soln. (0·1 *M*) was added to soln. of aluminium, zirconium or thorium salts and the excess titrated with 0·1 *M* $FeCl_3$, with 1 ml of 2% 3-hydroxy-2-naphthoic acid as indicator. The soln. was buffered to pH 4 and the titration carried out at 30° to 35°. As little as 10·8, 4·6 and 11·6 mg of Al, Zr and Th, respectively, can be determined. P. G.

4654. **Ultra-violet absorption spectrum of water stored in polyethylene bottles.** R. Delhez (Inst. de Chimie, Univ. de Liège, Belgium). *Chemist Analyst*, 1960, **49** (1), 20–21.—The presence of a trace impurity in re-distilled water stored in a polyethylene bottle is reported. The impurity shows an absorption max. at about 270 mμ and is susceptible to oxidation by H_2O_2. G. S. ROBERTS

4655. **Analysis of hydrogen - tritium mixtures by the thermal-conductivity method.** F. K. Heumann (Knolls Atomic Power Lab., Schenectady, N.Y.). *U.S. Atomic Energy Comm.*, Rep. KAPL-970, July, 1953. Decl. Mar., 1960. 20 pp.—The determination of ^3H in ^3H - H mixtures was investigated with the use of a thermal-conductivity cell. A study was made of the variables involved that may cause errors in the determination. These variables include the effect of certain gaseous impurities, variations in the bridge current, sample pressure, flow rate, and the effect of equilibration of ^3H - H mixtures. NUCL. SCI. ABSTR.

4656. **Deuterium analysis—a simple and precise method.** E. M. Arnett, M. Strem, N. Hepfinger, J. Lipowitz and D. McGuire (Dept. of Chem., Univ. Pittsburgh, Pa., U.S.A.). *Science*, 1960, **131**, 1680–1681.—Water samples (containing H_2O, ^3H_2O and H^3HO) are converted into H and H^3H by means of reaction with calcium hydride in a generator of simple design (described). With H as the carrier gas, the gases (H and H^3H) are passed into a gas chromatograph. No attempt is made to separate the isotopes as in other methods; the greater thermal conductivity of H^3H gives a peak that is linearly related to the ^3H content of the water in the range 0 to 10 moles %. Reproducibility depends on the calcium hydride surface, the carrier-gas flow and the avoidance of leaks during evacuation. R. A. HENDEY

4657. **The detection and determination of very small quantities of water by hygrophotography.** M. J. Sivadjian (Inst. Pasteur, Paris, France). *Anal. Chim. Acta*, 1960, **22** (3), 284–290 (in French).—The use of hygrophotography (*Brit. Abstr. C*, 1953, 526) is illustrated by the determination of water in aliphatic alcohols, plant leaves, soil and plastic film. A technique is described by means of which quant. results may be obtained. The amount of water corresponding to a given colour intensity is measured by pressing the film on the cellophane cover of a small flask containing water for 3 min., the flask being weighed on a microbalance before and after the exposure. A series of standards is then prepared by exposing the film to water and to five standard soln. of NaBr, and calculating the amount of water equivalent to each spot from the vapour pressure of the NaBr soln. W. T. CARTER

4658. **Coulometric determination of hydrogen peroxide with permanganate.** P. S. Tutundžić and M. M. Paunović (Inst. Phys. Chem. and Electrochem., Univ., Beograd, Yugoslavia). *Anal. Chim. Acta*, 1960, **22** (3), 291–295 (in German).—With the apparatus and technique previously described (Tutundžić and Mladenović, *Anal. Abstr.*, 1955, **2**, 2309, 2310) 1 to 5·5 mg of H_2O_2 can be determined with an accuracy of ±1%. The electrolyte is 0·2 *M* $MnSO_4$ in 7 *N* H_2SO_4, the electrolysis current is 8 to 10 mA, and the end-point is determined colorimetrically with ferroin or nitroferroin. The titration error shows a slight negative bias due to the catalytic decomposition of H_2O_2. This is minimised by using a small platinum anode and carrying out the titration as rapidly as possible. W. T. CARTER

4659. **Use of zeolites in gas chromatography. III. Separation and determination of helium, neon and hydrogen at normal temperature.** M. Krejčí and K. Tesařík (Lab. for Anal. of Gases, Acad. Sci., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 691–694 (in German).—Helium, Ne and H were separated on calcium aluminium silicate (mol. sieve 5Å) (*cf. Anal. Abstr.*, 1959, **6**, 1976). The elution vol. of these gases were measured. The chromatographic column consisted of an aluminium tube (8-mm diam.) filled with activated calcium aluminium silicate (109 g; 0·2 to 0·4-mm grain size); argon was used as the carrier gas and thermal conductivity for detection. J. ZÝKA

4660. **Mechanism and elimination of interferences in flame photometry. II. Ionisation and mutual interference of alkali elements.** Shouzow Fukushima (Fac. Sci., Osaka Univ., Nakanoshima, Japan). *Mikrochim. Acta*, 1960, (3), 332–343 (in English).—The interaction of binary mixtures of alkali metals is studied with a variety of techniques. The effects of atomisation of mixtures and of the injection into the flame of soln. of single elements from twin atomisers are reported, together with the differences in interference levels at different positions in the flame. The level of interference is least at the bottom of the flame. T. R. ANDREW

4661. **Determination of traces of oxygen in sodium metal by infra-red spectrophotometry.** H. J. de Bruin (Australian Atomic Energy Comm., Lucas Heights, N.S.W.). *Anal. Chem.*, 1960, **32** (3), 360–362.—The sample (0·8 to 1·0 g) is caused to react with *n*-pentyl chloride by a Wurtz reaction, when it is converted to NaCl contaminated with Na_2O. The Na_2O is then converted into Na_2CO_3 by atmospheric CO_2. The impure sodium chloride is then formed into a disc, and its extinction is measured at 11·38 μ, at which wavelength Na_2CO_3 absorbs strongly. Standards are prepared by evaporating mixtures of NaCl and Na_2CO_3 soln. to

dryness. Beer's law is obeyed over the range 0 to 300 p.p.m. of O. The coeff. of variation varies with the O concn., being $\simeq \pm 20\%$ at 20 p.p.m. (the lower limit of determination) and $\simeq \pm 4\%$ at 100 p.p.m.
J. H. WATON

4662. **Determination of potassium in mica by the perchlorate method.** M. L. Yashchenko and É. S. Varshavskaya (Lab. of Pre-Cambrian Geology, Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (3), 275–276.—The sample (0·5 g) is treated with 10 ml of HF and 25 to 30 ml of saturated oxalic acid soln. The soln. is evaporated to dryness, the residue is moistened with water, and the evaporation is repeated. The residue is then heated on a sand bath, finally at 250°, and treated first with 2 to 3 ml of conc. HNO_3 and then with 6 to 8 ml of $HClO_4$. The soln. is evaporated, but not to dryness, and the residue is boiled with 50 ml of water to complete dissolution of perchlorates. After filtration the soln. is treated with 3 to 4 ml of $HClO_4$ and evaporated nearly to dryness. The residue is treated with 5 to 10-ml portions ($\simeq$50 ml in all) of a soln. of 5 ml of $HClO_4$ in 1 litre of ethanol, and the $KClO_4$ is filtered off and dissolved in hot water containing $HClO_4$. The soln. is evaporated and the residue is treated with the $HClO_4$ - ethanol soln. in 3 to 5-ml portions ($\simeq$20 ml in all). The $KClO_4$ is dissolved in water, the soln. is evaporated and the residue is ignited at 350° and weighed.
G. S. SMITH

4663. **Conductimetric titration of caesium with antimony trichloride.** J. Havíř (Military Acad., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 695–700 (in German).—The conductivity of $SbCl_3$ and CsCl in conc. acetic acid was studied and a conductimetric determination of Cs was evolved. *Procedure*—Titrate the soln. of the sample, containing 200 to 300 mg of CsCl ($\simeq$6 mg of CsCl per ml) in anhyd. acetic acid, conductimetrically with 0·3 to 0·5 *M* $SbCl_3$. Calculate the result from the L-shaped curve. In the presence of sodium or potassium salts high results were obtained. The presence of Rb or Fe causes interreference.
J. ZÝKA

4664. **Radiochemical determination of caesium by the colorimetric determination of dipicrylamine.** A. M. Lefevre, J. F. Lefevre and A. Raggenbass (Dept. de Chim., Centre d'Études Nucléaires de Saclay, France). *J. Inorg. Nuclear Chem.*, 1960, **12** (3–4), 297–303 (in French).—The method is designed for the analysis of fission product soln. from which the interfering elements are first removed as carbonates and hydroxides. The pH of the soln. is then adjusted to $\simeq$9 and a two-fold excess of the magnesium salt of dipicrylamine (as a 3% aq. soln.) is added. After cooling for 3 to 5 hr. at 0° to 1°, the ppt. is filtered off and washed with ethyl ether and then dissolved in ethyl acetate, from which the Cs is extracted into 0·5 *N* HCl. The extinction of the organic phase is measured at 375 mμ and the content of dipicrylamine, and hence the recovery of Cs, is derived from a calibration curve. The content of radio-caesium in the HCl phase is determined by γ-counting.
G. J. HUNTER

4665. **Condensation product of benzoin and *p*-aminophenol, reagent for the quantitative determination of copper.** I. Matei and E. Cacea. *Bul. Inst. Politeh., Iaşi*, 1958, **4** (3–4), 175–180.—A Schiff base with reducing properties (attributed to the secondary alcohol of the benzoin) is prepared from benzoin and *p*-aminophenol. The reagent may be used in ethanolic solution at 50° to 70° to give a ppt. of Cu from $CuSO_4$ soln., which is recovered, washed and dried to constant weight at 105°.
J. L. PROSSER

4666. **Potassium pyrosulphate fusion technique. Determination of copper in mattes and slags by X-ray spectroscopy.** T. J. Cullen (United States Metals Refining Co., Carteret, N.J.). *Anal. Chem.*, 1960, **32** (4), 516–517.—The samples are fused with $K_2S_2O_7$ in borosilicate-glass beakers at a moderate temp. The cooled product is ground to about 200 mesh and then briquetted to give a uniform surface for X-ray analysis. In this way absorption and enhancement effects of the matrix are removed and no internal standard is required. The deviations from results obtained by chemical analysis vary from −0·27% to +0·15%.
K. A. PROCTOR

4667. **Characteristics of pulsed discharges for the spectrochemical analysis of impurities in brass.** J. McK. Nobbs, D. A. Sinclair and R. N. Whittem (Defence Standards Lab., S. Australia Branch, Adelaide). *Spectrochim. Acta*, 1960, **16** (3), 320–334.—A detailed investigation of the effect of peak current, mean pulse current, pulse duration and wave form on the spectral characteristics (sensitivity, line ratio, band-line strength and reproducibility) is reported. No single source setting will give max. sensitivity for all impurities in brass, but two satisfactory sets of pulse parameters are deduced having "half sine" (*L*-type) and "cut off" exponential (*R*-type) wave forms, respectively. The *L*-type (12 amp. peak current, 7·2 amp. mean current, 10 millisec. pulse duration) is preferred as it gives higher sensitivity and reproducibility, *viz*, As, limit of detection 0·011% (coeff. of variation 4·7%); Fe, 0·001% (10·0%); Ni, 0·0005% (7·6%); Pb, 0·0006% (9·5%); Sn, 0·001% (4·0%); and Mn, 0·0008% (6·8%).
P. T. BEALE

4668. **The extraction of silver as tri-*n*-butylammonium - silver saccharin.** M. Ziegler, H. Sbrzesny and O. Glemser (Anorg.-Chem. Inst. der Univ. Göttingen). *Z. anal. Chem.*, 1960, **173** (5), 411–414.—Silver can be determined in the presence of Bi, Cu, Fe or a 5000-fold excess of Pb by extraction as tri-*n*-butylammonium - silver saccharin, followed by pptn. as AgCl or Ag_2S. *Procedure*—To the test soln. containing $\gtrsim$15 mg of Ag and buffered at pH 4 to 5 with Na acetate and acetic acid add 1·5 ml of 25% aq. saccharin (Na salt) soln. and 8 ml of tributylammonium acetate (or add a soln. of tributylammonium saccharin). Extract (× 2) with dichloromethane and wash the organic layer with 15 ml of buffer soln. (pH 4 to 5). Dilute the organic layer with an equal vol. of methanol and add 3 to 4 ml of dil. HCl to precipitate AgCl. Filter off the ppt., and dry at 120°. Alternatively, add 5 ml of CS_2 to the organic phase, precipitate Ag_2S with H_2S, then filter off and wash the ppt. with CS_2 and dry at 130°.
P. D. PARR-RICHARD

4669. **The determination of silver and thallium in rocks by neutron-activation analysis.** D. F. C. Morris and R. A. Killick (Brunel Coll. of Technol., London, England). *Talanta*, 1960, **4** (1), 51–60.—Use of the radionuclides ^{110m}Ag - ^{110}Ag and ^{204}Tl obtained by irradiation for 1 month in Harwell pile BEPO permits determination of 0·01 p.p.m. of Ag and of Tl in a 1-g sample of rock; higher sensitivity is attainable in Harwell pile DIDO. The radiochemical separation, after addition of standardised carriers, involves digestion with HF, fuming with

$HClO_4$, and pptn. of Ag and Tl with HCl. The metal ions are then purified and counted as $AgIO_3$ and Tl_2CrO_4, respectively. Results correspond well with standard analyses. Errors introduced by nuclear reactions of Cd, In and Pb are insignificant.

J. P. STERN

4670. **Colorimetric determination [of gold] in Merrill tail solutions at the Hartebeestfontein gold mine.** C. R. Pugh and H. T. Tucker. *J. S. Afr. Inst. Min. Metall.*, 1960, **60** (8), 371–375.—The method described for the determination of Au in cyanide solution, which is sufficiently rapid for routine control of the Merrill precipitation process, has given results that are in excellent agreement with those obtained by fire assays. The Au is deposited on zinc dust, as in the Dowsett method (*Trans. Instn Min. Metall., London*, 1912–1913, **2**, 190), and digested in aqua regia. Sodium chloride is added and the soln. is evaporated nearly to dryness 3 times to eliminate HNO_3; *o*-tolidine reagent [0·01% in dil. HCl (1:100)] is added to develop the colour, and the extinction is measured within 15 min. in a model C Beckman colorimeter at 440 mμ.

J. M. JACOBS

4671. **Quantitative micro-analysis of gold.** F. A. Fer'yanchich. *Trudy Tsentr. N.-I. Gornorazved. Inst.*, 1959, (28), 147–169; *Ref. Zhur., Khim.*, 1960, (4), Abstr. No. 13,119.—The gold is first cleaned by boiling for 5 min. with HCl (1:1), washing with water, drying, beating to a thickness of ≃0·3 mm, cutting into small pieces, and repeatedly heating with HCl (1:1) till the soln. is completely colourless. The cleaned pieces are dried, beaten to a thickness of 0·1 mm, and again treated with HCl, washed and dried. A clean sample is dissolved in aqua regia in the presence of tartaric acid (**I**); the ppt. of AgCl, containing part of the Cu, Pb, Bi, Fe and Sb, is filtered off and treated with conc. aq. NH_3 in the presence of **I**. The insoluble residue, containing silicate particles and some gold, is filtered off and ashed and after repeated dissolution its gold content determined as described earlier (Fer'yanchich, *Trudy Inst. Nigrizoloto*, 1947, **16**, 293). A large excess of a neutral soln. of ammonium acetate is added to the ammoniacal soln. (to pH 8 or 9), and metallic silver is pptd. with a hot soln. of hydrazine sulphate, filtered off, ignited at about 700° to 750°, and weighed. From the acid soln. Au is pptd. by hydrazine sulphate, carrying with it Se and Te (quant. if their content is ⩾0·02 and 0·03%). To remove Au, the ppt. is dissolved in aqua regia, a boiling soln. of 2 g of ammonium oxalate in 90 ml of water is added, Au is filtered off after 24 hr., and washed with HCl (1:20). The filtrate is strongly acidified with HCl, and the Se, Te and dissolved Au are pptd. by 0·05 g of $CuSO_4.5H_2O$ and 5 ml of a soln. of 20 g of tin in 100 ml of conc. HCl. The ppt. is dissolved in aqua regia, Au is pptd. with ammonium oxalate soln. and the soln. is boiled, the Au is filtered off after 24 hr., united with the main bulk of the metal, ignited at 700° to 800°, and weighed. Selenium and Te are pptd. from the filtrate in the same way, the ppt. is dissolved in HNO_3 (1:1), and $SnCl_2$ added to the soln.; Se forms an orange ppt., and Te a black ppt. These elements may be separately determined polarographically. From the first acid filtrate from Au, Se and Te, united with the filtrate from the pptn. of Ag, after neutralisation with aq. NH_3 to pH ⩾8, the sulphides of Cu, Pb, Bi and Fe are pptd. and filtered off after 30 to 60 min., and the sulphides of As and Sb are pptd. by boiling the filtrate acidified with acetic acid. To purify the ppt., it is dissolved in aqua regia, **I** is added, then aq. NH_3 till the soln. is slightly alkaline; the soln. is saturated with H_2S, and the pptd. sulphides of Cu, Pb, Bi and Fe are combined with the first ppt.; the filters are ashed, the residue is fused with $K_2S_2O_7$, the melt is dissolved in HCl (1:20), and the sulphides of Cu, Pb and Bi are pptd., filtered off after 10 to 15 min. and ashed. The residue is evaporated first with 2 or 3 drops of HNO_3 (1:1) and then with 1 or 2 drops of HCl (1:1), and Cu, Pb and Bi are polarographed in a basal soln. of salts of acetic acid and **I**. In the filtrate from the Cu, Bi and Pb pptn., Fe is oxidised and determined by photometry as the sulphosalicylate. The filtrates from the thio bases are oxidised with H_2O_2, the excess of H_2O_2 is destroyed by boiling and by the action of $KMnO_4$ in dil. HCl, the soln. is boiled, H_2S is passed, the Sb_2S_3 is immediately filtered off, and dissolved by heating in 1 or 2 drops of conc. HCl; Sb^V is reduced to Sb^{III} with thiourea, and Sb is determined by the pyridine iodide method. After removing Sb_2S_3, the filtrate is oxidised with $KMnO_4$ and As is determined by the hypophosphite method, correcting for its content in the reagents. In a separate sample, Mn is determined by titration as $KMnO_4$, and S by pptn. as $BaSO_4$ after decomposition of the sample with aqua regia and removal of impurities by electrolysis with a mercury cathode.

C. D. KOPKIN

4672. **Determination of beryllium.** L. M. Moiseeva and N. N. Kuznetsova. USSR Pat. 124,194 (20.11.59).—5:5-Dimethylhexane-2:4-dione (**I**) is used as reagent. Fuse a sample of ore (≃0·5 to 2 mg of Be) with KHF_2, extract the melt with H_2SO_4 and evaporate till no more SO_3 is evolved. Dissolve the residue in 100 ml of hot water, cool, precipitate Sn with H_2S, add 50 to 100 ml of 5% EDTA (disodium salt) soln., adjust the pH to between 7 and 8, add **I** soln. (15 to 20 ml for each mg of Be: excess does not interfere), allow the ppt. to settle (3 to 4 hr.), filter on a sintered-glass filter, wash the ppt. several times with cold water, and dry it to const. wt. at 50°. The conversion factor for Be is 0·03096.

C. D. KOPKIN

4673. **Analysis of beryllium and beryllium oxide. I. Determination of iron.** J. O. Hibbits, W. F. Davis and M. R. Menke (G.E.C. Aircraft Nuclear Propulsion Dept., Evendale, Ohio, U.S.A.). *Talanta*, 1960, **4** (1), 61–66.—Tervalent iron is separated from Be by extraction from HCl soln. into *cyclo*hexane containing tri-*n*-octylphosphine oxide (**I**) and determined spectrophotometrically as the 1:10-phenanthroline complex. The accuracy is within ±3% or ±3 μg of Fe, whichever is greater. Silicon (5 mg), Sb (1), Ga (1), Mo (1), W (1), Te (0·1) and U (0·1 mg) do not interfere. *Procedure*—To the sample containing ≃100 μg of Fe add citric acid (1 g), adjust the soln. to 6 *N* in HCl, add bromine water (4 drops) and then 0·01 *M* **I** in *cyclo*hexane (25 ml). Shake, remove the aq. phase, and add 3 ml of the dry organic phase to *iso*propyl alcohol (**II**) (15 ml). Add 3% quinol in **II** (1 ml) and then 3% 1:10-phenanthroline in **II** (2 ml). Set aside for 2 hr. and measure the extinction (in 2-cm cells) at 510 mμ against a blank soln. Determine the Fe content from a standard curve.

J. P. STERN

4674. **Radiometric methods for the determination of magnesium and calcium in Portland cement.** C. T. Brown, J. E. Howes, jun., T. S. Elleman, C. W. Townley and D. N. Sunderman (Battelle Memorial

Inst., Columbus, Ohio). *U.S. Atomic Energy Comm.*, Rep. BMI-1415, Feb., 1960. 13 pp.—Two methods have been developed. Both methods employ, as precipitant, standard $(NH_4)_2HPO_4$ soln. labelled with ^{32}P. In the presence of aq. NH_3, this reagent precipitates $MgNH_4PO_4$ or $Ca_3(PO_4)_2$ from a soln. containing Mg^{2+} or Ca^{2+}. The reduction in the radioactivity level of the labelled phosphate soln. after precipitation serves as a measure of the phosphate reacted and thus as a measure of the amount of Mg or Ca present. Studies have been made of the effects of reagent concn., aq. NH_3 concn. and other experimental variables. The interference of other elements normally present in Portland cement and its raw materials has been determined. The concn. ranges for highest accuracy have been found to be 5 to 15 mg of MgO per 100 ml and 15 to 30 mg of CaO per 50 ml.

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4675. **2-NN-Di(carboxymethyl)aminomethylquinizarin as a new metallochromic indicator for calcium.** S. Stankoviansky, V. Podaný, F. Jassinger and P. Majer (Dept. Anal. Chem., Komenský Univ., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (4), 265–274.—The preparation of a new chelatometric indicator, by condensation of iminodiacetic acid with quinizarin in the presence of formaldehyde, is described. Its colour change at pH 12 was studied spectrophotometrically. *Procedure for Ca*—Dilute the soln. of the sample containing $\geq$1200 mg of Ca^{2+} with H_2O to $\simeq$100 ml, add 2 *N* NaOH (5 to 6 ml) and 0·01 g of the indicator (1% in KCl) and titrate with 0·1 *M* EDTA (disodium salt), with stirring, till the colour changes from pale blue to intense blue - violet. The titration can be carried out in the presence of small amounts of Pb^{2+}, Hg^{2+}, Sn^{2+}, Bi^{3+}, Sb^{3+}, Al^{3+}, Co^{2+}, Tl^+ and Ni^{2+}, and of large amounts of Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, CrO_4^{2-} and acetate. The presence of Mg^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+} and phosphate causes interference; interference of Mn and Fe can be avoided by the addition of triethanolamine (3 to 4 ml of 25% triethanolamine soln. per mg of Mn^{2+} or Fe^{3+}) and that of Cu by the addition of KCN (2 to 3 g of KCN per 100 ml of soln.). J. ZÝKA

4676. **The partition of metallic 8-hydroxyquinoline compounds between water and organic solvents. VI. Experiments on the hydroxyquinolinate complexes of beryllium, strontium and barium.** F. Umland, W. Hoffmann and K.-U. Meckenstock (Inst. f. Anorg. Chem., Tech. Hochsch., Hannover). *Z. anal. Chem.*, 1960, **173** (3), 211–227 (in German).—The behaviour of Be, Sr and Ba towards 8-hydroxyquinoline was examined photometrically in aqueous and chloroform soln. in the presence and absence of *n*-butylamine. For comparison, the 8-hydroxyquinoline complexes of Mg and Ca were investigated. The structure of the resulting di- and tri-hydroxyquinolinates is discussed in relation to the position of the elements in the Periodic Table, and the anomalous behaviour of Be is considered. P. G.

4677. **Co-crystallisation of ultramicro quantities of alkaline-earth elements with potassium rhodizonate. Determination of radio-barium in sea water.** H. V. Weiss and Ming G. Lai (U.S. Naval Radiological Defence Laboratory, San Francisco, Calif.). *Anal. Chem.*, 1960, **32** (4), 475–478.—The co-crystallisation of a number of elements with potassium rhodizonate (**I**) is reported, and it is shown that quant. recovery of alkaline-earth elements from soln. 10^{-1} to 10^{-4} *M* is obtained on crystallisation of 50% of added **I**. To the sample of sea water (1 vol.) is added **I** soln. (2 vol. of 1·2%) and, after thorough mixing, ethanol (1 vol.) is added. After setting aside the mixture for 5 min. the crystals of **I** are filtered off. Radioactive Ba and other co-crystallised fission products in, *e.g.*, sea water, are then determined with a scintillation spectrometer. The percentage recovery of 11 other radioactive elements is reported, and a procedure for separation of ^{140}Ba from the other active elements is described. T. R. ANDREW

4678. **Decomposition of radium sulphate with ion-exchange resins and the separation of lead-210 and polonium from radium.** W. Dedek (Inst. für angew. Radioaktivität, Leipzig). *Z. anal. Chem.*, 1960, **173** (5), 399–411.—In the separation of radium-D (^{210}Pb) from $RaSO_4$, radioactive $BaSO_4$ was taken as a model substance for the $RaSO_4$. After stirring for 30 min. at 60° with a 1:1 mixture of a strong anionic resin (Wofatit SB) (OH^- or ClO_4^- form) and a strong cationic resin (Wofatit P) (H^+ form), <1% of the $BaSO_4$ remained unadsorbed. To separate ^{210}Pb from Ba, the equilibrated mixture was poured on to a column containing a little more cationic resin (to remove traces of Ba eluted along with the SO_4^{2-}) and the SO_4^{2-} were eluted with *N* NaOH; $\leq$98% of the SO_4^{2-} was recovered. Barium and ^{210}Pb were then eluted with *N* $HClO_4$ and the eluate was passed through a column of Wofatit KPS 200, from which ^{210}Pb was eluted with *N* HCl and Ba with 6 to 8 *N* HCl; the recovery of ^{210}Pb was 95 to 98%. To separate Po from $BaSO_4$, the mixture was dissolved in hot conc. H_2SO_4, diluted to 7 *N* to re-precipitate $BaSO_4$ and heated to redissolve adsorbed Po; ^{210}Pb was largely pptd. with $BaSO_4$, while some ^{210}Bi remained in soln.; Po is easily separated from traces of ^{210}Pb and ^{210}Bi. Barium was separated from Ra by elution with 0·15 *M* EDTA at pH 6·2. P. D. PARR-RICHARD

4679. **Use of unithiol for volumetric determination of zinc.** L. A. Vol'f (S. M. Kirov Leningrad Textile Inst.). *Zavod. Lab.*, 1960, **26** (3), 271–272.—The soln. (10 ml) of Zn^{2+} (0·01 *N*) is mixed with 5 ml of a buffer soln., containing 350 ml of 25% aq. NH_3 and 54 g of NH_4Cl per litre, and 10 drops of a 0·4% soln. of Eriochrome black T in ethanol and titrated with 0·01 *N* unithiol (Na 2:3-dimercaptopropanesulphonate). Interference is caused by Co, Cd, Hg, Mn, Pb, Ni, Cu, Ca, Mg, Cr and Ag, but not by alkali metals or <5 mg of Fe per litre. The colour change is from red to blue. G. S. SMITH

4680. **Simple apparatus for the coulometric titration and determination of zinc by the generation of potassium ferricyanide.** P. K. Agasyan. *Vestn. Moskov. Univ.*, 1959, (6), 156–162.—It is shown that smaller quantities of Zn^{2+} than those indicated in the literature can be determined by means of potentiometric and amperometric end-point indication. By these methods Zn^{2+} concn. of 180 to 3000 μg in 50 ml of soln. were accurately determined. A. BURWOOD-SMITH

4681. **X-ray spectrographic determination of zinc in aluminium alloys.** A Buccheri and V. Ferreira Alves (Inst. de Pesquisas Tecnol., São Paulo, Brazil). *ABM (Bol. Assoc. Brasil. Metais), São Paulo*, 1960, **16** (59), 413–422.—Zinc emits K_α rays (λ = 1·44 A) when excited by voltages >10kV. The intensity of these rays is proportional to the amount of Zn present and the technique is suitable for the determination of Zn in aluminium and its alloys. Samples

of known Zn content are treated with HNO_3 and HF and calcined at 950° to form the oxides of the metals, which are then excited with 25 kV (current 20mA) in a suitable X-ray tube with a tungsten anode. The rays are passed through a LiF crystal analyser into a Geiger counter fitted with an automatic recorder. A standard curve is constructed relating counts per sec. with % of Zn in the sample. The method was applied to samples containing 0·02 to 6% of Zn and gave reproducible results with a coeff. of variation of $\pm$ 1·1% (120 measurements). Two standard samples of alloys, containing 1·50 and 0·44% of Zn, gave results of 1·48 and 0·45%, respectively, by this method.

G. H. FOXLEY

4682. **Chromatographic determination of metallic impurities (copper, iron, nickel, cobalt) in zinc and zinc salts.** I. R. Bellobono (Ist. Tec. Ind. "Stanislao Cannizzaro," Rho, Milan). *Chim. e Ind.*, 1960, **42** (3), 259–262.—Concn. of 0·0005% of Cu, Fe, Ni and Cu can be determined by co-pptn. followed by paper-chromatographic separation, and photodensitometric, colorimetric and polarographic analysis. The metal sample (100 g) is dissolved in a slight excess of dil. acid (1 : 4), and 0·5 g of Mn^{2+} (as $MnSO_4$) is added. After being made up to $\simeq$ 1 litre, the soln. is cooled, and 30 ml of bromine water is added. Free acid is neutralised to precipitate the Zn as zincate. Further treatment with bromine water, filtration, and dil. acid, and concentration yields a Zn- and Mn-free soln. of other metals present, which are determined by the methods mentioned above. A specific example of co-pptn. is studied by radiochemical methods, with ^{60}Co as tracer.

C. A. FINCH

4683. **Separation of cadmium from uranium, cobalt, nickel, manganese, zinc, copper, titanium and other elements by cation-exchange chromatography.** F. W. E. Strelow (Nat. Chem. Res. Lab., S. African Council for Sci. and Ind. Res., Pretoria). *Anal. Chem.*, 1960, **32** (3), 363–365.—The ions are adsorbed on a column of AG 50W-X8 resin (22 cm × 1·15 cm) from a soln. $>$ 0·2 *N* in HCl. Tervalent gold, Pt^{IV}, Se, V^V and Mo are washed through the column with 0·2 *N* HCl. The Cd, together with Be, Sn^{IV}, Li and Na, is eluted with 225 ml of 0·5 *N* HCl at a flow rate of 2·0 to 2·5 ml per min., leaving U, Co, Ni, Mn, Zn, Cu, Ti, Fe, Al, Y, Zr, Th, Cs, alkaline-earth and rare-earth metals on the column. A separation of Be from Cd can be achieved on a 35-cm column. Interference is shown by Bi, Ag, Hg^I, Pb, Tl^I and W. Sulphate up to 0·1 *N* may be tolerated if no cations forming insol. sulphates are present.

J. H. WATON

4684. **Polarographic determination of thallium and lead in cadmium.** V. A. Tsimmergakl and Z. A. Krasnova. *Ukr. Khim. Zhur.*, 1959, **25** (4), 501–504; *Ref. Zhur., Khim.*, 1960, (7), Abstr. No. 26,358.—The method depends on the extraction of Tl from the fused cadmium with a mixture of $ZnCl_2$ and NH_4Cl and subsequent polarography; the greater part of the Cd is then distilled off in a current of H, and Pb and other non-volatile impurities are dissolved and polarographed. *Procedure*—Fuse 1 to 20 g of cadmium turnings with a mixture of potassium and ammonium acetates to remove Zn (*cf. Anal. Abstr.*, 1960, **7**, 1289); wash the salts from the residue, fuse it with a mixture of 1·5 g of $ZnCl_2$ (1 ml of 75% w/v soln.) and 1 g of NH_4Cl (free from Pb), stirring for 10 min. Cool, treat the melt with hot water, evaporate the soln. twice with HNO_3 (3 ml each), add hydrazine sulphate and water, and evaporate; add 0·5 g of citric acid and 5 ml of 25% aq. NH_3, add gelatin soln. or 0·2 ml of a 0·5% soln. of carboxymethylcellulose, a little Na_2SO_3 (or ascorbic acid), dilute to 10 ml and polarograph, determining Tl by the method of additions. Prepare a blank simultaneously with cadmium not containing Tl. With a lead content $>$ 0·01%, dissolve part of the metallic cadmium (0·5 g), after removing Tl, in 10 ml of HCl and 0·5 ml of HNO_3, evaporate twice to dryness with HCl, treat with 0·1 *N* HCl, add 0·2 ml of a 0·5% soln. of carboxymethylcellulose, dilute to 10 ml, pass a stream of H and polarograph, determining Pb and Cu by the method of additions. Carry out a blank at the same time. With a lead content $<$ 0·01%, heat 10 to 20 g of cadmium (after removal of Tl) in a porcelain boat in a quartz tube in a stream of H in a tube furnace at 650° to 700°, and treat the residue (0·3 to 0·5 g) as described above.

C. D. KOPKIN

4685. **Colorimetric determination of metals by means of Reinecke salt. I. Determination of mercury.** J. Weyers (Wydz. Farm., Akad. Med., Kraków). *Chem. Anal., Warsaw*, 1960, **5** (1), 95–99.—Mercury in inorganic and organic compounds may be quickly determined by pptg. with Reinecke salt in an acid medium. The ppt. formed is filtered off and dissolved in anhyd. pyridine giving a violet-red colour which is measured photometrically. When the mercury content is between 5 and 50 mg per ml the Beer-Lambert law is obeyed.

M. MORAN

4686. **Rapid colorimetric determination of mercury by tin(II) - strong phosphoric acid reduction method.** Toshiyasu Kiba, Ikuko Akaza and Osamu Kinoshita (Dept. of Chem., Univ., Kanazawa, Japan). *Bull. Chem. Soc. Japan*, 1960, **33** (3), 329–335 (in English).—The sample (containing $>$ 50 μg of Hg) is heated in a round-bottomed flask with 10 to 20 ml of a prepared mixture of $SnCl_2.2H_2O$ (50 g) and conc. H_3PO_4 ($d \simeq 1·7$, 250 g) in a rapid stream of CO_2, whereby the liberated mercury vapour is carried into a mixture of 0·1 *N* $KMnO_4$ (10 ml) and 10% aq. H_2SO_4 (10 ml). The Hg^{2+} thus formed are determined by the usual dithizone - $CHCl_3$ method, the extinction of the organic layer being measured in a 1-cm cell at 517 mμ. Digestion of the sample in an inert atmosphere eliminates the error caused by volatilisation of mercury in the usual digestion methods. Trace amounts of Hg in soln. (as chloride or sulphate) must be concentrated by co-pptn. with $Fe(OH)_3$ or CdS, and the ppt. (collected on an asbestos disc) digested with the Sn^{2+} - H_3PO_4 mixture; if CdS is used, a larger vol. of $KMnO_4$ soln. should be present in the absorbent. The procedure is applicable to the rapid determination of Hg in organic fungicides and pharmaceutical preparations, *e.g.*, merbromin, ethylmercury phosphate, methoxyethylmercury chloride and thiomersalate, without special pre-treatment.

W. J. BAKER

4687. **Coulometric oxidation of boron.** H. Robson and T. Kuwana (Res. Lab., Esso Standard Oil Co., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 567–568.—Boron may be stripped from deposits on platinum by electrolytic dissolution into *N* KOH. Results obtained by this coulometric oxidation were in fair agreement (within 20%) with results obtained by titration of the stripped soln. The degree of stripping varied from 50 to 90%, and this was attributed to poor contact between the B and the platinum base.

T. R. ANDREW

4688. **Determination of boron in borohydrides and organoboron compounds by oxidation with trifluoroperoxyacetic acid.** R. D. Strahm and M. F. Hawthorne (Redstone Arsenal Res. Div., Rohm & Haas Co., Huntsville, Ala., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 530–531.—The sample (containing 2 to 6 mg of B) is placed in a test-tube, methyl cyanide (1 ml) is added, a reflux-condenser is fitted, and the tube is cooled in an ice bath for a few minutes. Trifluoroperoxyacetic acid (**I**) (2 ml) is cautiously added through the top of the condenser and, after any initial reaction has subsided, the tube is heated in a boiling-water bath for 5 to 60 min., according to the stability of the sample. For samples requiring long heating, a further 1 ml of **I** is added after 30 min. When decomposition is complete the soln. is washed into 50 ml of water and boiled gently for a few minutes before titrating the boric acid in the usual manner, after its conversion into mannitoboric acid. The reagent is prepared by adding H_2O_2 (90%) (1 ml) to methyl cyanide (9 ml), cooling in ice and cautiously adding, while swirling, trifluoroacetic anhydride (6·2 ml). Good results are reported for 29 compounds.

T. R. Andrew

4689. **Separation and determination of aluminium in plutonium - aluminium alloys.** F. J. Miner, R. P. Degrazio, C. R. Forrey, jun., and T. C. Jones (Rocky Flats Plant, Dow Chemical Co., Denver, Colo., U.S.A.). *Anal. Chim. Acta*, 1960, **22** (3), 214–220 (in English).—The elements are separated by passing the sample soln., in 8 *N* HCl, through an anion-exchange resin; Pu^{IV} is retained and Al is determined in the eluate. *Procedure*—Dissolve the sample (containing ≃5 mg of Al) in 8 *N* HCl (2 ml). Then slowly add conc. HNO_3 (2 ml). Transfer the soln. to a column (25 cm × 2·2 cm) of Dowex 1-X4 (chloride form) and elute with 8 *N* HCl (60 ml) at 2 ml per min. To the eluate add 0·1 *M* EDTA (disodium salt) (5 ml) and 0·1% bromocresol green soln. (2 drops). Neutralise with 12 *N* NaOH, add acid buffer soln. (108·9 g of Na acetate and 2·3 ml of glacial acetic acid per litre) (5 ml) and 0·2% xylenol orange soln. (5 drops), and titrate with 0·02 *M* Zn acetate to a purple end-point. Iron and Cu do not interfere; Cr must be oxidised to chromate; Ni (>600 p.p.m.) interferes seriously and must be removed by pptn. with dimethylglyoxime before titrating. The analysis of a synthetic alloy soln. containing 5 mg of Al gave a mean recovery of 4·92 mg and a standard deviation of ±0·10 mg; the corresponding values for the volumetric 8-hydroxyquinoline method were 4·93 mg and ±0·08 mg, respectively. The analysis of 22 alloys containing ≃1% of Al gave a standard deviation of ±0·012%.

W. T. Carter

4690. **Determination of thallium(I) with iodate in the presence of mercuric ions and with iodate and permanganate via bromide.** Bechu Sharma (Hindu Univ., Benares, India). *Bull. Chem. Soc. Japan*, 1960, **33** (3), 277–279 (in English).—Milligram amounts of Tl^+ can be determined accurately by oxidation, at 25°, to Tl^{3+} with 0·1 *N* KIO_3 in 1 to 2 *N* HCl soln. containing Hg^{2+} (≃20 ml of 8% aq. $HgCl_2$). A direct or reverse amperometric titration is made, the end-point being detected by the dead-stop method. Accurate results are also obtained by the amperometric titration of Tl^+, *e.g.*, thallous acetate soln., with KIO_3 or $KMnO_4$ in 3 to 5 *N* HCl containing 2 to 3 g of KBr. In all titrations a potential of 0·1 V is applied across the electrodes.

W. J. Baker

4691. **Photometric determination of thallium in the ultra-violet [region].** G. V. Efremov and K. N. Stolyarov. *Uch. Zap. Leningr. Gos. Univ.*, 1959, (272), 99–104; *Ref. Zhur., Khim.*, 1960, (7), Abstr. No. 26,251.—Thallium is determined in soln. and wastes from the production of non-ferrous metals and H_2SO_4 by a method based on the oxidation of I^- by Tl^{3+} with subsequent determination of the iodine on a u.v. photometer [*Ref. Zhur., Khim.*, 1956, (8), Abstr. No. 22,704]. Tervalent Tl is first concentrated by co-pptn. with $Fe(OH)_3$ and heavy metals are removed by pptn. with Na_2CO_3. To 1 g of sample add 10 g of Na_2SO_4 and 5 ml of conc. H_2SO_4, heat carefully for 30 min., fuse for 1 hour at 350° to 370°, add 0·2 to 0·3 g of NaF to remove SiO_2 and heat for a further 30 min. (if a crust forms on the melt, add H_2SO_4 to the cooled mixture). Cool, add 75 ml of water, heat, filter, and wash the residue with water. To the filtrate add NaOH soln. till a ppt. begins to form, dissolve the ppt. in HCl, heat twice with aq. Br to oxidise Tl^+ to Tl^{3+}, and add aq. NH_3 in slight excess. Collect the hydroxide ppt. containing the Tl^{3+}, dissolve it in dil. HCl, evaporate the soln. to 3 to 5 ml, add H_2SO_3 to reduce Tl^{3+} to Tl^+, dilute to 50 ml, and add a saturated Na_2CO_3 soln. till the heavy-metal carbonates are completely pptd. Filter immediately, wash the ppt. with water (× 3 or 5) and make the filtrate up to 100 ml. To 10 ml of this soln. add 1 to 3 ml of aq. Br to oxidise Tl^+, heat for 3 min., add 0·2 ml of a 20% soln. of phenol in glacial acetic acid to destroy excess of Br, cool rapidly with water, set aside for 3 min., add 5 ml of 0·2% KI soln., make up to 25 ml and measure the extinction immediately. Beer's law is obeyed for concn. of 5 to 100 μg of Tl in 25 ml of soln. The sensitivity of the determination is 0·2 μg of Tl per ml.

C. D. Kopkin

4692. **Photometric determination of cerium with sodium 1:2-dihydroxybenzene-3:5-disulphonate (tiron).** R. Püschel (Med.-chem. Inst., Univ., Graz, Austria). *Mikrochim. Acta*, 1960, (3), 344–351 (in German).—In alkaline soln. (pH 9·5 to 11·5) Ce^{III} reacts with tiron giving a wine-red colour (absorption max. at 510 mμ), which is stabilised by the presence of ascorbic acid. Iron, Al and Ti interfere, but the procedure is unaffected by Th or rare-earth elements. The faintly acid soln. is reduced with ascorbic acid (5 mg). Tiron (30 mg) is then added, followed by sufficient water to dissolve the reagents, methanol (4 ml) and buffer soln. (54 g of NH_4Cl and 350 g of aq. NH_3 to 1 litre) (1 ml). After dilution to 10 ml with water the soln. is set aside for 1 hr. and the extinction is measured at 510 mμ. Recoveries of 24 to 131 μg of Ce are within 4 μg. The procedure may be scaled up by a factor of 5; recoveries of from 0·34 to 1·34 mg of Ce are then within ±0·03 mg. The reaction may also be applied to the detection of Ce by spot reaction, in the absence of Fe.

T. R. Andrew

4693. **Simultaneous extraction and spectrophotometric determination of cerium with 2-thenoyltrifluoroacetone.** Shripad M. Khopkar and Anil K. De (Dept. Chem., Jadvapur University, Calcutta 32, India). *Anal. Chem.*, 1960, **32** (4), 478–480.—Quadrivalent Ce is extracted from faintly acid soln. into benzene as the 2-thenoyltrifluoroacetone (**I**) complex. The efficiency of extraction is 100% at pH 5·4, falling to 80% at about pH 4·5 and pH 6·2. The orange - red extract shows an absorption maximum at 410 mμ but, owing to the high absorption of **I** at this wavelength, measurements are best

made at 450 mμ. Beer's law is obeyed at 450 mμ for concn. of 3 to 40 μg of Ce per ml, and 1 mg of Ce^{IV} (in 25 ml) gives an extinction of about 0·7. The interference of 14 ions has been studied.

T. R. ANDREW

4694. **Rapid method for the spectrographic determination of rare-earth elements in monazites and cerium minerals.** O. Brieux de Mandirola (Com. Nac. Energ. Atom., Buenos Aires). *An. Asoc. Quím. Argentina*, 1959, **47** (2), 90–98.—A Hilger model E 492 quartz spectrograph in the range 3100 to 6000 A, with graphite electrodes under a p.d. of 250 V (d.c.) is used; cyanogen bands are suppressed with $Ba(NO_3)_2$. The sample (10 mg) is mixed with $Ba(NO_3)_2$ (120 mg), filled into a cup-shaped depression in the anode and dried for 30 min. at 80°. No chemical separations are necessary. The spectral lines used, and the sensitivities and errors involved in the determination of each element are tabulated. All the rare-earth elements, except ytterbium, can be determined with errors generally less than ±10%.

E. C. APLING

4695. **Electro-deposition of actinide elements at tracer concentrations.** R. F. Mitchell (Reactor Monitoring Center, Tracerlab, Inc., Wright Ave., Richmond, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 326–328.—In the method described, the elements are deposited on platinum discs from an electrolyte of NH_4Cl - HCl, usually ≃5 ml. The discs are removed from the soln., washed with ethanol and flamed. Determination of the deposited elements is carried out by scintillation counting. The procedure produces deposits that are adherent and uniformly distributed over the plate.

K. A. PROCTOR

4696. **Measurement of the purity of graphite and heavy water.** H. Hering. Commissariat à l'Énergie Atomique, Paris, Rep. CEA-10, Feb., 1959. 32 pp.—The determination of the change in neutron capture cross-section of graphite from sample to sample is determined by an oscillation method in the ZOE reactor, or by measuring the attenuation of a neutron flux in the subcritical system Mireille. Methods of determining total ash, B, H, Cl, Na, Ca, Fe, Mo, Ti, V, Sm, Eu, Dy, S, Co and Cd are described and mean results are given. The methods for sampling are indicated. The isotopic analysis of heavy water is carried out by i.r. absorption measurements. Chemical purity is evaluated by electrical conductivity measurements. B, Na, Mg, K, Cr, Mn, Ni, Cu and Cd are determined by spectrographic methods, and Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ by chemical methods; finally, sensitive pH measurements are described.

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4697. **Studies in qualitative inorganic analysis. XV. The detection of carbon monoxide.** O. B. Hayes (Handsworth Tech. Coll., Birmingham 21, England). *Mikrochim. Acta*, 1960, (3), 366–368 (in English).—A soln. of $PdCl_2$ (0·1% in 0·5% HCl) is advocated for detecting CO evolved from some qual. tests (*e.g.*, heating oxalate with H_2SO_4). A distinctive blue - grey colour is given, readily distinguishable from the black colour given with H or H_2S or the brown stain given by SO_2. In use, a drop of the reagent soln. is spotted on to a filter-paper, which is held in the evolved gases. The evolution of H_2S from sulphides or of halogens from halides would interfere with the reaction, and these compounds must be decomposed first by gentle heating with dil. H_2SO_4.

T. R. ANDREW

4698. **Determination of traces of carbon monoxide in hydrogen.** G. Ciuhandu (Inst. of Hygiene, Timişoara). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **7** (4), 569–571.—The method is based on the degree of reduction of silver *p*-sulphamoylbenzoate (**I**) at 0°, at which temp. the reduction due to H is negligible. *Procedure*—The apparatus is as described by Ciuhandu and Krall (*Rev. Chim., Bucharest*, 1959, **10**, 531), except that the gas-receiver capacity is increased to 5 litres. The mixed gases are bubbled through the reagent (1 vol. of 0·1 *M* $AgNO_3$ + 1 vol. of 0·1 *M* **I** + 0·5 vol. of *M* NaOH) contained in a narrow test-tube, cooled in ice, at the rate of ≃10 ml per min. At a concn. of CO of 0·1% the colourless soln. changes sharply to yellow. At concn. <0·01%, colour appears after the passage of several hundred ml. A passage of 2 litres is necessary for the detection of 0·001%, while 0·0005% can be detected in 5 litres. (*Cf. Anal. Abstr.*, 1960, **7**, 2114.)

H. SHER

4699. **Polarographic determination of thiocyanate ion.** R. A. Plowman and I. R. Wilson (Dept. of Chemistry, Univ. of Queensland, Brisbane, Australia). *Analyst*, 1960, **85**, 222–225.—The method was developed for determining SCN^- in acid soln. containing also HCN, H_2O_2 and SO_4^{2-}. It was found that 0·1 *N* $HClO_4$ is a satisfactory supporting electrolyte for the determination. Potentials at which the diffusion current due to SCN^- approximates to a limiting value extend from +0·325 to +0·350 V *vs.* a S.C.E. Under the conditions described, CN^- do not produce an anodic wave, and dissolved O and H_2O_2 do not influence the diffusion current of SCN^-. The mechanism of the reaction was investigated experimentally.

A. O. JONES

4700. **Analysis of chemically pure silicon by radioactivation.** M. Bădănoiu, M. Fiti and C. Măntescu (Inst. Atom. Phys., Acad. R.P.R., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **7** (4), 573–579.—The method is based on the comparison of the level of induced radioactivity in a standard sample of known composition and in the unknown sample. *Procedure*—The impurities are identified by resolution of the disintegration curves of the isotopes formed by induced radioactivity to give the typical half-life values ($T_{\frac{1}{2}}$). Irradiation times were chosen to give resolution of curves as large as possible so that they would not contain more than 2 or 3 active isotopes. In order to cover the possible impurities, *viz*, Al, Ag, Mg, Zn, Cu, As, Pt, Fe and B, and simplify the disintegration curves, the above elements are divided into 3 groups, *viz*, the isotopes with low, medium and high values of $T_{\frac{1}{2}}$. For group I satisfactory saturation was obtained by irradiation of 0·1 g of Si for 30 min. in a flux (10^{11} neutrons per sq. cm per sec.) of a thermal reactor. The disintegration curve from this gave $T_{\frac{1}{2}}$ = 2·2 min. corresponding either to ^{108}Ag or ^{28}Al and $T_{\frac{1}{2}}$ = 150 min. corresponding to ^{31}Si. A γ-spectrum of the sample lacked the characteristic line $E\gamma$ = 1·78 MeV of ^{28}Al, from which it was deduced that the $T_{\frac{1}{2}}$ of 2·2 min. was due to ^{108}Ag. The absence of the other isotopes of low $T_{\frac{1}{2}}$ values, *i.e.*, of Mg. Al, Zn and Cu, was evident from the disintegration curve. To identify the elements of the second group, the irradiation was carried out under the same conditions of flux density, but for 5 hr., and measurements of activity were taken 20 hr. afterwards to eliminate those of low $T_{\frac{1}{2}}$. Only ^{76}As appeared on the curve for $T_{\frac{1}{2}}$ = 26 hr. Similarly the third group was separated by irradiation under the same conditions for 40 hr., but the activity readings were

taken only after 300 hr., and $T_{\frac{1}{2}}$ of 4·3 and 45 days were obtained corresponding to ^{193}Pt and ^{59}Fe, respectively. Having identified impurities as Ag, As, Pt and Fe, portions of the sample were then irradiated as before, but in each case accompanied by a standard amount of the impurity already found in that group. From the two disintegration curves obtained in each case, the corresponding activities of the elements being sought are deduced for $T = 0$, and the amount of impurity present is calculated in direct proportion to the activity of the standard quantity taken. Values (%) given are $Ag = 6{\cdot}2 \times 10^{-5}$, $As = 9{\cdot}4 \times 10^{-3}$, $Pt = 4{\cdot}6 \times 10^{-3}$, and $Fe = 7{\cdot}6 \times 10^{-3}$, with errors of $\pm 10\%$.

H. SHER

4701. **Photometric determination of traces of boron in silicon.** F. A. Pohl, K. Kokes and W. Bonsels (A.E.G. Forschungs-Inst., Frankfurt, Germany). *Z. anal. Chem.*, 1960, **174** (1), 6–15 (in German).—Details are given of a procedure applicable to the determination of as little as 10^{-7} % of B in silicon. The silicon sample (1 to 20 g) is treated with bromine in a special apparatus (described in detail) at 750° and the silicon tetrabromide, after dissolution in CCl_4, is hydrolysed, H_3BO_3 is distilled off as methyl borate, and B is subsequently determined photometrically with curcumin. Results for contents of B greater than 10^{-6} % have a precision of ± 10 to 20%, while the error at levels of 10^{-7} % may be ± 20 to 50%.

T. R. ANDREW

4702. **Neutron activation analysis of iodine in silicon.** Tadashi Nozaki, Hideo Baba and Hidemaro Araki (Nippon Telegraph and Telephone Publ. Corp., Tokyo, Japan). *Bull. Chem. Soc. Japan*, 1960, **33** (3), 320–322 (in English).—From 0·005 to 5 p.p.m. of iodine in silicon can be determined in $\simeq 1$ hr., with a chemical yield of 50 to 70%, by the procedure given. The sample (0·8 g), after neutron irradiation, is fused with KOH (10 g) containing several milligrams of KI as carrier, and the melt is then digested with 5 *N* H_2SO_4 (100 ml) containing a few milligrams of NaCl and KBr as hold-back carrier. A soln. of $NaNO_2$ is added to the product and the liberated iodine is distilled (two distillations are made) into a dil. soln. of Na_2SO_3, from which it is extracted into xylene and then back-extracted into an aq. Na_2SO_3 soln. From this soln. AgI is pptd., weighed and counted (with a gas-flow 2π-counter if the concn. of iodine is $<0{\cdot}01$ μg). The accuracy was confirmed by use of ^{131}I formed by neutron irradiation of Te diffused in silicon. With a 2π-counter the limit of detection is 0·002 μg at a neutron flux of 6×10^{11} per sq. cm per sec. Contamination of the ppt. with radioactive Si is negligible.

W. J. BAKER

4703. **Polarographic behaviour of the heteropoly acids of molybdenum. II. Determination of silicon in aluminium alloys.** K. Grasshoff and H. Hahn (Inst. f. anorg. Chem., Univ., Kiel). *Z. anal. Chem.*, 1960, **173** (3), 198–208 (in German).—A "single sweep" cathode-ray polarograph is used. The silicon in a 50-mg sample of alloy is converted into molybdosilicate. For alloys containing 0·05 to 0·5% of Si, the maximum deviation from the mean was <5%. The method is claimed to be suitable for serial determinations and to be sufficiently rapid for routine use.

P. G.

4704. **Rapid method for the gravimetric determination of silica.** P. Pássera, L. Garzón Ruipérez and J. Salas Sanceledonio (Lab. de la Empresa Roldan, S.A. Aceros, M.T.S.). *Inf. Quim. Anal.*, 1960, **14** (2), 38–40.—The sample (*e.g.*, of quartz) is fused with NaOH and Na_2O_2 and extracted with H_2O. The extract is treated with excess of HCl, and then boiled with dil. H_2SO_4 (1:1) until the SiO_2 is pptd. in copious flocks. After cooling to $\simeq 60°$, a 1% soln. of gelatin is added and the ppt. is filtered off, washed with 10% HCl and ignited at $\simeq 1000°$, to yield SiO_2 of high purity, which is weighed.

L. A. O'NEILL

4705. **Titrimetric determination of soluble silica as molybdosilicic acid.** Takeo Takahashi and Shingo Miyake (Inst. of Ind. Sci., Univ. Tokyo, Japan). *Talanta*, 1960, **4** (1), 1–7 (in English).—The quant. reduction of molybdosilicic acid by 0·01 *N* $FeSO_4.(NH_4)_2SO_4$ and 1% oxalic acid or by 0·01 *N* $SnCl_2$ and 6 *N* H_2SO_4 permits sol. SiO_2 (>10 μg) to be determined spectrophotometrically or potentiometrically. The reaction involves the transfer of four electrons. The accuracy is $\simeq \pm 2{\cdot}5\%$. *Spectrophotometric procedure*—To an aliquot (0·25 to 3 ml, containing 10 to 100 μg of SiO_2) add 6 *N* H_2SO_4 (3 drops) and 2·5% $(NH_4)_6Mo_7O_{24}$ soln. (1 ml). After several minutes, add either 5% oxalic acid (5 ml) and 0·01 *N* $FeSO_4.(NH_4)_2SO_4$ (>1·5 ml), or 6 *N* H_2SO_4 (5 ml), water (10 ml) and 0·01 *N* $SnCl_2$ (>1 ml). Dilute to 25 ml and after a short interval measure the extinction at 680 mμ. *Potentiometric procedure*—To the soln. (1 ml, containing $\simeq 40$ μg of SiO_2) add 6 *N* H_2SO_4 (3 drops) and 2·5% $(NH_4)_6Mo_7O_{24}$ soln. (1 ml). After several minutes add 6 *N* H_2SO_4 (5 ml), dilute with water to 25 ml and titrate with 0·01 *N* $SnCl_2$ at 25° to 30°; allow a few minutes to elapse before the potential measurement after adding each 0·02 ml of titrant, as the change in potential is slow near the end-point.

J. P. STERN

4706. **Study of the surface acidity of silicates and aluminosilicates by titration in non-aqueous media.** J. J. Fripiat, G. Vancompernolle and A. Servais (Inst. Agron., Univ., Louvain, Héverlé, Belgium). *Bull. Soc. Chim. France*, 1960, (2), 250–259.—A titrimeter is described in which solid materials are titrated in a jacketed vessel with sodium methoxide by high-frequency titration (sometimes in the presence of indicators). Circuits are given for the high-frequency titrimetry and for the automatic addition from the burette at a rate of 1 or 2 drops per min. The solvents used are benzene, acetone - benzene (4:1) and ethylenediamine - benzene (1:1). A study of the titration curves enables acidity of Hammett function <11 [SiOH, $Al(H_2O)_6^{3+}$ and non-hydrated H^+] and between 11 and 34 (H_3O attached to SiOH, H^+ or K^+) to be distinguished, determined in μ-equiv. per g and related to the specific surface, for silica gel in various states of hydration, montmorillonite, two cracking catalysts, partially hydrated alumina and two kaolinites.

E. J. H. BIRCH

4707. **Quantitative drop method of determining germanium with phenylfluorone.** B. M. Lipshits and G. K. Smirnova (M. I. Kalinin Inst. of Non-Ferrous Metals and Gold). *Zavod. Lab.*, 1960, **26** (3), 273–274.—A drop (0·005 to 0·01 ml) of phenylfluorone soln. (50 mg dissolved in 100 ml of 96% ethanol containing 0·5 ml of 6 *N* HCl) is placed on filter-paper followed by one drop of the soln. to be tested (3 to 6 *N* in HCl) and one drop of 6 *N* HNO_3. The intensity of the pink colour appearing in the presence of Ge is compared with that of standards. The method was tested with satisfactory results over the range 2·7 to 1080 μg of Ge

per drop. Small amounts (5%) of Fe^{3+} do not interfere; the effect of larger amounts can be masked by the addition of PO_4^{3-}. G. S. SMITH

4708. **Determination of germanium in germanium-rich material.** F. Csapo and H. Repetschnig (Lab. der Zinkhütte, Bleiberger Bergwerks-Union, Arnoldstein, Kärnten, Austria). *Z. anal. Chem.*, 1960, **173** (4), 273–275 (in German).—The Ge is isolated by extraction with CCl_4 from 8 *N* HCl soln. and determined by titrating mannitogermanic acid with standard alkali soln. *Procedure*—Fuse the sample, containing >50 mg of Ge, with Na_2O_2 (2·5 g) in a nickel crucible. Extract the melt with water (100 ml), add CCl_4 (250 ml), cautiously neutralise with conc. HCl and add sufficient excess to give an 8 *N* soln. Extract the Ge into the CCl_4 layer and extract twice more with CCl_4 (50 ml). Combine the CCl_4 extracts and extract with water (4 × 20 ml). Combine the aqueous extracts and dilute to 100 ml. Take an aliquot containing $\simeq 20$ mg of Ge, dilute to 50 ml, neutralise to pH 6·2 with *N* NaOH, with a pH meter, add mannitol (15 g) and titrate to pH 6·2 with 0·02 *N* NaOH that has been standardised against pure GeO_2.
W. T. CARTER

4709. **Rapid volumetric method for the determination of tin in simple solders.** H. Nechamkin (Pratt Inst., Brooklyn, New York, U.S.A.). *Chemist Analyst*, 1960, **49** (1), 20.—With simple Sn - Pb solders the iodimetric titration method can be speeded up by dissolving the solder in an O-free atmosphere. It is then not necessary to reduce the Sn^{IV} to Sn^{II} since the presence of Pb ensures that all the Sn is in the bivalent form. Substantial amounts of Sb or Cu interfere. G. S. ROBERTS

4710. **Quantitative colorimetric determination of lead and zinc.** A. M. Lukin, G. S. Petrov and K. A. Smirnova. USSR Pat. 121,282 (15.7.59).—The preparation from aminoazobenzene and diazotised 4-nitroanilino-2-arsonic acid of 4-(2′-arsono-4′-nitrophenyl)diazoaminobenzeneazobenzene and its use as a reagent for Pb and Zn is described together with methods of overcoming interferences.
C. D. KOPKIN

4711. **Isotopic composition of lead in pegmatitic felspars.** E. J. Catanzaro and P. W. Gast (Lamont Geol. Observatory, Columbia Univ., New York). *Geochim. et Cosmoch. Acta*, 1960, **19** (2), 113–126.—An ion-exchange method is used for separating microgram quantities of Pb from rocks and minerals, following the dissolution of the sample with HF and $HClO_4$. Lead is selectively adsorbed on Dowex-1 resin from a *N* HCl soln. and eluted with 8 *N* HCl; the eluate is evaporated to dryness and the residue is taken up in HNO_3; PbS is pptd. with H_2S. Isotope abundance measurements are made on 10 to 20 μg of this PbS. The total Pb content of the sample is determined spectrographically and a thick-source α-scintillation counter is used to determine the equivalent U content.
R. A. HOWIE

4712. **Separation of lead-212 from thorium.** T. T. Gorsuch (U.K.A.E.A., The Radiochemical Centre, Amersham, Bucks., England). *Analyst*, 1960, **85**, 225–226.—De-Acidite FF anion-exchange resin, of water regain 1·0 to 1·5 and of −100 to +200 mesh, washed free from fines, was equilibrated with 2 *N* HCl. A thorium soln. (10 g of Th in 50 ml of 2 *N* HCl) was passed through the column (10 cm × 1·5 cm), which was then washed with 25 ml of 2 *N* HCl. The lead was eluted rapidly and completely with water and a decay graph indicated its purity. A. O. JONES

4713. **Complexometric determination of titanium in *n*-butyl titanate.** Ya. I. Chulkov (V. I. Lenin All-Union Electrotech. Inst.). *Zavod. Lab.*, 1960, **26** (3), 272–273.—The sample ($>0·3$ g) is decomposed by heating in 2 ml of conc. HCl and the soln. is diluted to 250 ml. Any Fe^{3+} must be oxidised to Fe^{3+}. To determine Fe, an aliquot (50 ml) of the soln. is mixed with 50 ml of water and titrated at 40° to 50° with 0·05 *M* EDTA (disodium salt), in the presence of 0·1 ml of 10% ethanolic salicylic acid soln. as indicator. To determine Ti, each of two 50-ml aliquots is mixed with 50 ml of water and, if the content of Fe in the sample is $<0·8\%$, with 2·0 ml of a 0·05 *M* soln. of Fe^{3+}. The soln. at 40° to 50° are each treated with 0·1 ml of salicylic acid soln. and then, dropwise, with 30% H_2O_2 soln. One soln. is then titrated with 0·05 *M* EDTA (disodium salt) to a brownish-yellow colour and treated with a further 2 ml of the titrant; the colour is then yellow with a green tint. The other soln. is titrated until the colour matches, dropwise addition being necessary near the end-point, which, in opaque soln., can be located by a photo-electric method. This titration gives the sum of Fe and Ti.
G. S. SMITH

4714. **Phase analysis of titanium alloys.** R. B. Golubtsova. USSR Pat. 120,925 (6.7.59).—In the phase analysis of titanium alloys by selective anodic dissolution, the electrolyte used contains 3 g of succinic acid and 5 ml of HCl (sp. gr. 1·19) in 1 litre of methanol, and the process is carried out at a current density of 0·1 amp. per sq. cm for 1·5 hr. without cooling. The intermetallic phase $TiCr_2$ is quant. pptd. as a powder free from titanium salts and may be analysed microchemically. Titanium - chromium alloys containing up to 45% of Cr may be analysed. C. D. KOPKIN

4715. **Thiomalic acid as reagent for zirconium.** Suseela B. Sant and Bharat R. Sant (Dept. of Chem., Univ., Toronto, Ont., Canada). *Anal. Chem.*, 1960, **32** (3), 379–380.—The Zr soln. must be $>0·2$ *N* in HNO_3 or $>0·1$ *N* in HCl. Thiomalic acid is added as a 2% aq. soln., and the ppt. is digested at 80° to 90° for $\simeq 30$ min. After being set aside for 1 hr., the ppt. is filtered off on a No. 42 paper, washed with hot water and ignited to ZrO_2. In the presence of Hg^{II}, the ppt. must be filtered off immediately after digesting, since Hg gives a ppt. on standing. In the presence of Th, which tends to co-precipitate with Zr, larger amounts of reagent are added to a 0·2 *N* HNO_3 soln. of the metals, and the ppt. is washed with 0·2 *N* HNO_3 and then with hot water. Bismuth must be removed as Bi_2S_3, and free H_2SO_4 (or SO_4^{2-} in the presence of HCl or HNO_3) must be absent. J. H. WATON

4716. **Use of organic reagents in inorganic analysis. XI. Gravimetric determination of zirconium with maleanilic acids.** S. K. Datta [Victoria (Government) College, Coochbehar, India]. *Z. anal. Chem.*, 1960, **174** (1), 30–35 (in English).—The procedure devised for Th (*cf. Anal. Abstr.*, 1960, **7**, 4724) has been found equally applicable to the determination of Zr. Recommended maleanilic acids are those derived from 2:5-dichloroaniline, *o*- and *p*-toluidine, *o*- and *p*-anisidine, 1- and 2-naphthylamine, *m*-phenylenediamine and *o*-tolidine. Precipitation is generally complete at $\simeq 0·5$ pH unit less than that used for Th. Interferences are as given for Th.
T. R. ANDREW

4717. **Spectrometric study of the reaction of zirconium with methylthymol blue.** V. F. Luk'yanov and E. M. Knyazeva. *Zavod. Lab.*, 1960, **26** (3), 263–265.—The soln. containing Zr is treated first with 5 ml of conc. HCl and evaporated to ≃1 ml, and then with 2 ml of a 0·1% aq. soln. of methylthymol blue and diluted to 25 ml with 0·5 *N* HCl. The extinction is measured at 580 mμ in a 1-cm cell. With concn. between 10 and 100 μg of Zr in 25 ml the Beer - Lambert law is obeyed. Most cations in concn. ten times that of Zr do not interfere. Interference is caused by Bi^{3+} and Fe^{3+} (which can be reduced to non-interfering Fe^{2+} by ascorbic acid) and also by >100 μg of Sn^{4+} and Ti^{4+}. To determine Zr in alloys containing Cu and Ti, the sample (0·2 g) is dissolved in conc. HCl and an aliquot of the diluted soln. is treated with Al^{3+} (to serve as a collector) and then with aq. NH_3 together with H_2O_2 when Ti is present. The pptd. $Zr(OH)_4$ is dissolved in HCl, the soln. is evaporated to ≃1 ml and the procedure is continued as described above. Satisfactory results were obtained with alloys containing between 0·05 and 0·90% of Zr.

G. S. Smith

4718. **Spectrophotometric method for the determination of zirconium with mandelic acid.** V. M. Peshkova, N. V. Mel'chakova and A. B. Urazekova. *Vestn. Moskov. Univ.*, 1959, (6), 150–155.—The method described by Hahn and Weber (*Anal. Abstr.*, 1956, **3**, 2039) has been studied. The optimum conditions for the pptn. of Zr are a ratio of Zr to mandelic acid of 1:5 and a standing time of 3 hr. Titanium at a ratio of Ti to Zr up to 10:1 and Th at a ratio up to 5:1 can be complexed with sulphosalicylic acid. The ammonium complex is shown to have the formula $(NH_4)_4Zr(C_8H_6O_3)_4$.

A. Burwood-Smith

4719. **Titrimetric determination of zirconium in "red mud."** A. Schneer (Inst. Phys., Hungarian Acad. Sci., Budapest). *Chem. Anal., Warsaw*, 1960, **5** (1), 79–84.—Zirconium was determined after pptn. as Zr tetramandelate by titration either with $KMnO_4$ (for 2 to 20 mg of Zr) or $K_2Cr_2O_7$ (for 0·1 to 5 mg of Zr). This proved more accurate than the gravimetric method and when applied to a sample of red mud containing ≃0·1% of Zr gave errors up to ±6%. Amounts of Zr >0·1 mg can also be determined in minerals and industrial wastes.

W. B. Miaskowski

4720. **Determination of zirconium in uranium fission alloys.** H. B. Evans, A. M. Hrobar and J. H. Patterson (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 481–483.—Two procedures are presented for the separation of Zr from other constituents of fission alloy (0·1% of Zr, 0·01% of Nb, 3·4% of Mo, 2·6% of Ru, 0·5% of Rh and 0·3% of Pd in uranium) before the photometric determination as the alizarinsulphonate. In one method, pptn. with cupferron followed by several pptn. with aq. NH_3, is used, and, in the other, preliminary separation with aq. NH_3 followed by pptn. with *p*-chloromandelic acid is used. Recoveries on 22 synthetic samples containing from 0·1 to 0·4 mg of Zr (and 10 to 1000 mg of U) were within ±1% of the added Zr, except for four samples containing 1000 mg of U, when the error reached 1·8%.

T. R. Andrew

4721. **EDTA titration of zirconium, hafnium and thorium in their alloys with tungsten or in tungsten metal.** E. Lassner and R. Scharf (Metallwerk Plansee A.-G., Reutte, Tirol, Austria). *Chemist Analyst*, 1960, **49** (1), 22.—Before Zr and Hf can be titrated with EDTA they must be separated from W, since all three metals are masked by the common masking reagents. *Procedure*—Dissolve the alloy (5 g for samples containing 0·5 to 5% of Zr, Hf or Th) in HF and HNO_3 and evaporate the soln. to dryness. Fuse the residue with $K_2S_2O_7$ and dissolve the melt in H_2O. Add 10% KOH soln. and filter off the pptd. Zr, Hf and Th. Dissolve the ppt. in HNO_3 (1:1) at 90° and filter, and to an aliquot of the diluted filtrate add a measured excess of EDTA (disodium salt) soln. Adjust the pH to 2 to 3 with dil. aq. NH_3, add xylenol orange indicator (1:100 with solid KNO_3) and back-titrate with $Bi(NO_3)_3$ or $Th(NO_3)_4$ soln. The mean absolute error is +0·01% (7 determinations).

G. S. Roberts

4722. **Determination of zirconium-95 plus niobium-95 by anion-exchange separation from other fission products.** A. C. Leaf (General Electric Co., Hanford Atomic Products Operation, Richland, Wash.). *U.S. Atomic Energy Comm.*, Rep. HW-62188, Oct., 1959. 16 pp.—The ^{95}Zr and ^{95}Nb are adsorbed on to Dowex-1 resin (F^- form) from a HF soln. of the fission products. The resin is counted directly by using a 3-in. NaI(Tl) well crystal and a γ-scintillation spectrometer. Yields of >99·5% are obtained. The activity levels of the major fission products ^{106}Ru, ^{137}Cs and ^{144}Ce are reduced by >95%.

Nucl. Sci. Abstr.

4723. **Extraction of thorium with thenoyltrifluoroacetone. Effect of acetic acid.** G. Goldstein, O. Menis and D. L. Manning (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 400–404.—The presence of acetic acid enhances the extraction of Th^{4+} from aq. soln. with a soln. of thenoyltrifluoroacetone in CCl_4 or *iso*butyl methyl ketone. This effect is due to the formation of an adduct of the Th chelate with acetic acid in the org. solvent, and of a Th - acetate complex in the aq. soln. Reactions are suggested and approx. equilibrium constants are calculated. The factors to be considered in the selection of the org. solvent are discussed.

J. H. Waton

4724. **Use of organic reagents in inorganic analysis. X. Determination of thorium with maleanilic acids.** Sachindra Kumar Datta [Victoria (Government) College, Coochbehar, India]. *Z. anal. Chem.*, 1960, **174** (1), 23–29 (in English).—Seventeen maleanilic acids have been prepared and examined as pptn. reagents for Th. Those prepared from *p*-anisidine, 1- and 2-naphthylamine, *m*-phenylenediamine and *o*-tolidine precipitate Th quant. from soln. at pH 2·7 to 4·5. The ppt. are not stoicheiometric and must be ignited to ThO_2. Thorium may be determined in the presence of Ca, Ba, Sr, Al, Zn, Mg, Ti and the rare-earth elements; double pptn. is necessary in the presence of Ni, Co, Cr and U; Fe, Pb, Hg, Ce^{IV}, Zr and Pt interfere; Ce^{IV} appears to be tolerated up to a CeO_2 to ThO_2 ratio of at least 8:1. The soln. is adjusted to pH 2, 1% ammonium acetate soln. (3 ml) is added, the vol. is adjusted to 50 ml, then the soln. is heated to 80° and a 1% soln. of the reagent in 80% ethanol is added. After 1 min. the ppt. is filtered off, washed with ethanol and ignited to ThO_2. The reagents prepared from *m*-phenylenediamine, 1- and 2-naphthylamine and *o*-tolidine can be used for determining as little as 2·5 mg of ThO_2.

T. R. Andrew

4725. **Analytical aspects of some azo dyes from chromotropic acid. VIII. Spectrophotometric determination of thorium with 1:8-dihydroxy-2-(5-, 6- and 8-sulphonaphthylazo)naphthalene-3:6-disulphonic acids [SNADNS -5, -6 and -8].** Sachindra Kumar Datta (Victoria Gov. Coll., Coochbehar, W. Bengal, India). *Z. anal. Chem.*, 1960, **173** (5), 369–377 (in English).—Three naphthylaminesulphonic acid derivatives are compared as reagents for Th; the complexes with SNADNS-5 and -6 give max. absorbance at 610 mμ and that with SNADNS-8 at 161 mμ. The reactions are stoicheiometric and follow Beer's law; the optimum pH for reaction are 3·5, 3·02 and 3·2, and the sensitivities are 0·106, 0·16 and 0·17 μg per sq. cm, respectively. The colours develop rapidly and are stable for 24 hr.; temp. has little effect up to 60°. Copper, Sn and Ca interfere slightly, Fe^{III}, Ce^{IV}, Zr, Au, PO_4^{3-}, F^- and oxalate more seriously.

IX. Spectrophotometric determination of thorium with 1:8-dihydroxy-2-(2-hydroxy-4-sulphonaphthylazo)- and 1:8-dihydroxy-2-(8-hydroxy-3:6-disulphonaphthylazo)-naphthalene-3:6-disulphonic acids [OH-SNADNS and DSNADNS]. Sachindra Kumar Datta. *Ibid.*, 1960, **173** (5), 377–382 (in English).—Two further dyes, OH-SNADNS and DSNADNS, give complexes with Th with absorption max. at 610 and 620 mμ, respectively; the optimum pH for reaction are 2·6 and 2·0, respectively. Beer's law is obeyed for concn. up to 30 and 20 mg of Th per litre, respectively; the sensitivities are 0·16 and 0·1 μg per sq. cm. Copper, Sn, Fe^{II}, Ca, Ba, Ni, Co and U interfere slightly, Fe^{III}, Ce^{IV}, Zr, Au, PO_4^{3-} and F^- more seriously.

P. D. PARR-RICHARD

4726. **A new rapid method of determining thorium in presence of zirconium, iron, lanthanum, uranium, and other heavy metals.** R. Přibil and K. Burger (Chem. Inst., Czech Acad. of Sci., Prague, Czechoslovakia). *Talanta*, 1960, **4** (1), 8–12.—This is a version, in German, of a paper published in *Magyar Kém. Foly.*, 1959, **65**, 204; *cf. Anal. Abstr.*, 1960, **7**, 447.

4727. **Characteristics of alginic acid as a cation exchanger and its application to the separation of thorium(IV) and cerium(III) ions.** Takeo Takahashi and Shingo Miyake (Inst. Ind. Sci., Univ. Tokyo, Yayoi-cho, Chiba). *Bull. Chem. Soc. Japan*, 1959, **32** (12), 1324–1327 (in English).—The cation-exchange properties of alginic acid are, as expected, intermediate between those of a weakly acidic (Amberlite IRC-50) and strongly acidic (Amberlite IR-120) resin. Both Ce^{III} and Th^{IV} are retained on a column of alginic acid at pH 2 to 2·5. Tervalent Ce is eluted with HNO_3 (<0·1 *N*) and Th^{IV} can be eluted subsequently with *N* HNO_3 (*cf. Anal. Abstr.*, 1960, **8**, 1703).

T. R. ANDREW

4728. **Polarographic characteristics of ammonium ion and ammonia.** C. J. Nyman, J. R. Ragle and P. F. Linde (Dept. of Chem., Washington State Univ., Pullman, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 352–355.—A polarographic study of NH_4^+ in 0·1 *M* tetramethylammonium iodide and/or hydroxide reveals that the electrode process is diffusion-controlled, and is thus consistent with the formation of an amalgam at the mercury electrode. The process is irreversible in acid soln., but is reversible in alkaline soln., the wave being due to a 1-electron reduction to an amalgam.

J. H. WATON

4729. **Direct iodimetric determination of hydroxylamine.** M. Bartušek (Inst. Anal. Chem., Univ. Brno, Czechoslovakia). *Z. anal. Chem.*, 1960, **173** (3), 193–194 (in German).—Aq. soln. of hydroxyammonium chloride are titrated with iodine soln. in the presence of MgO, with starch soln. as indicator. The method is suitable for the determination of 5 to 30 mg of the salt. The error is <2%. P. G.

4730. **Analysis for industry [organic reductants in the determination of phosphorus by the molybdenum blue method].** A. M. G. Macdonald. *Ind. Chem.*, 1960, **36**, 134–136.—A literature survey is presented. 1-Amino-2-naphthol-4-sulphonic acid is chiefly useful in biochemical work, hydrazine is extremely adaptable, metol is the least sensitive to the effects of SiO_3 and Cl^-, and ascorbic acid is probably the most sensitive. (42 references.) S.C.I. ABSTR.

4731. **A chemi-chromatographic micro-method of determining phosphorus.** R. Antoszewski and J. S. Knypl (Dept. Plant Physiol., Univ., Łódź, Poland). *Mikrochim. Acta*, 1960, (3), 325–331 (in English).—The dimensions of a spot of quinoline molybdophosphate, produced when a drop of soln. containing PO_4^{3-} is applied to a paper impregnated with quinoline molybdate, are related to the P content. The area of the spot is roughly proportional to P content up to 130 sq. mm for 11 μg of P. The area of spot is measured, either after reduction to molybdenum blue, or by a photographic method involving u.v. irradiation of the paper over an underlying measuring grid.

T. R. ANDREW

4732. **Hydrolysis and determination of phosphates.** R. E. Shoup. *Wat. & Sewage Wks*, 1959, **106**, 354–355.—Results of an extensive study carried out on the quant. and qual. determination of phosphates are outlined. Investigations revealed no satisfactory alternative to the use of the molybdenum blue colour complex for the quant. determination of phosphorus and related compounds. The techniques employed in the standard colorimetric determination of phosphates with ammonium molybdate and stannous chloride and the factors affecting the reaction are discussed; the effects of various factors on the development of colour during this reaction are also considered. A detailed procedure for the rapid spectrophotometric determination of total ortho-, meta- and poly-phosphates is described. All forms of phosphate are hydrolysed rapidly to orthophosphate by vigorous boiling for several minutes at pH ≃0·55 in the presence of free Cl or Br. Excess of halogen must be removed, before addition of the stannous chloride, by agitation and addition of a small amount of sodium thiosulphate. WAT. POLLUT. ABSTR.

4733. **Application of metal-specific indicators to precipitation titrations. VI. The rapid direct volumetric determination of phosphate ion with standard cerium(III) solution after the separation of interfering ions with the aid of ion-exchange resins.** R. Püschel and E. Lassner (Brüder Reininghaus, G.m.b.H., Graz, Austria). *Z. anal. Chem.*, 1960, **174** (1), 1–3 (in German).—The interference of polyvalent cations in an earlier method (*cf.* Lassner *et al.*, *Anal. Abstr.*, 1960, **7**, 3200), is overcome by preliminary passage of the soln. (pH 1 to 2) through a cation-exchange resin (Lewatit S100 or Merck I).

VII. A new rapid direct method for the determination of microgram quantities of orthophosphate. R. Püschel. *Mikrochim. Acta*, 1960, (3), 352–356 (in German).—After passage through a cation-exchange resin (H^+ form), the soln. (10 to 20 ml)

containing PO_4^{3-} (20 to 400 μg) may be titrated at pH 6 with 0·0015 *M* $Pb(NO_3)_2$, with 4-(2-pyridylazo)resorcinol as indicator. In the presence of SO_4^{2-} the titration is carried out with 0·002 *M* $Ce_2(SO_4)_3$ at pH 6 after addition of 0·5 to 1 g of hexamine; Eriochrome black T is used as indicator. A standard deviation of $\pm 2{\cdot}3$ μg of PO_4^{3-} is claimed for the Pb^{II} titration (18 determinations) and of $\pm 1{\cdot}8$ μg of PO_4^{3-} in the Ce^{III} procedure (30 determinations). A determination may be made in 5 min. or less. T. R. ANDREW

4734. **Method for the separation of orthophosphate from other phosphate compounds.** B. Hagihara and H. A. Lardy (Inst. for Enzyme Res., Univ. of Wisconsin, Madison, U.S.A.). *J. Biol. Chem.*, 1960, **235** (3), 889–894.—The method of Berenblum and Chain (*Brit. Abstr. AI*, 1938, 212) for the separation of inorganic orthophosphate from phosphoric esters and anhydrides is adapted to a reverse-phase silicone-treated Celite column procedure that allows the investigation of many samples simultaneously. The molybdophosphoric acid is formed in the presence of aq. $HClO_4$ and is adsorbed on the column while the esters pass through. The acid is then extracted with hexanol or heptan-2-ol. The extraction is affected by the kind of acid present, by the pH, and by the rate of flow. The presence of methanol improves the extraction, particularly at higher pH values. Reducing agents, which interfere with the extraction, are destroyed by pre-treatment with Br. J. N. ASHLEY

4735. **The use of oscillographic polarography in quantitative analysis. XI. Detection and determination of arsenic, antimony and tin in mixtures.** J. Doležal and K. Janáček (Dept. Anal. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 885–889 (in German).—The depolarisation effects of As, Sb and Sn in electrolytes containing HCl and chlorides of alkali metals were studied and a new oscillopolarographic method for the detection and determination of these elements in the presence of each other was developed. The results were evaluated with the use of the method of comparative titration. Characteristic marked cutins on the oscillopolarographic curves $dV/dt = f(V)$, suitable for quant. purposes, were obtained in a medium of *M* HCl in the following concn. ranges of the elements studied—As 1×10^{-4} *M* to 5×10^{-4} *M*, Sb and Sn $0{\cdot}5 \times 10^{-4}$ *M* to 2×10^{-4} *M*. The method can be used for the determination of As, Sb or Sn in mixtures, after the preliminary separation from the sample in the form of thio salts, after the decomposition of the sample and reduction with SO_2 or by distillation. For the determination of As in biological materials the preliminary decomposition and preparation of the sample with the use of a modified Bambach method (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 265) is recommended. J. ZÝKA

4736. **Determination of antimony and arsenic in the presence of each other.** R. Kemka and J. Klučík (Inst. Hyg., Ind. Diseases, Bratislava, Czechoslovakia). *Pracovní Lékařství*, 1960, **12** (2), 74–79.—Phenylfluorone is used to precipitate Sb^{III}. *Procedure*—To the sample containing 10 μg to 7 mg of Sb add conc. HNO_3 (20 to 50 ml) and conc. H_2SO_4 (2·5 ml), heat, and to the dark soln. add H_2O_2 (30%) dropwise till the soln. is colourless. Repeat the procedure till the liquid remains colourless or slightly yellow. Add a satd. soln. of ammonium oxalate (5 ml) and heat again to remove oxides of N. Cool and dilute to 25 ml. To 1 to 5 ml add H_2SO_4 (10%) (4 ml), H_2O (4 ml) and Na_2SO_3 soln. (25%) (1 ml); reduce by boiling for 15 min. under reflux. Dilute to 10 ml, add gelatin soln. (1%) (1 ml) to disperse the ppt. and add the soln. of phenylfluorone (0·05%) (0·5 ml). After 30 min., measure the extinction at 530 mμ. Compare with a calibration curve. If determining Sb in the presence of As, reduce Sb as described above and to the cooled soln. add phenylfluorone soln. (0·5 ml) without gelatin. Filter off the pink - orange ppt., wash with 1·5 *N* H_2SO_4 and determine As in the filtrate after distillation. J. ZÝKA

4737. **Gravimetric determination of bismuth with dimethylglyoxime.** P. F. Lott and R. K. Vitek (Sch. of Mines and Metall., Univ. of Missouri, Rolla, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 391–393.—Bismuth is pptd. quant. as yellow $Bi_2O_2(C_4H_6N_2O_2)$ when an acetone soln. of dimethylglyoxime is added to a Bi soln. at pH 11 in the presence of EDTA (disodium salt) and KCN; the ppt. is filtered off and dried at 105° to 125°. The EDTA serves to prevent the pptn. of basic bismuth salts, and KCN and EDTA together effectively mask Al, As, Ba, Cd, Ca, Co, Cu, Pb, Mg, Hg, Ni, Pd, Pt, Ag, Sr, W and Zn; Sb, Cr, Fe, Mn, Th, Sn, U and Zr must be absent. J. H. WATON

4738. **Electrometric estimation of bismuth.** V. D. Anand, B. N. Prasad and A. A. Amani (Hindu Univ., Benares, India). *Bull. Chem. Soc. Japan*, 1959, **32** (12), 1387–1389 (in English).—Bismuth trichloride (3 to 100 mg) in anhydrous ethanol, methanol or acetone soln. may be titrated potentiometrically, by means of a platinum - tungsten or bismuth - tungsten electrode system, with thiourea, phenylthiourea, *p*-tolylthiourea or urea. Because of the insolubility of urea in acetone it is not possible to use this medium for titrations with urea. Two end-points are recorded, at $2BiCl_3.3X$ and at $BiCl_3.3X$ (where X is the complexing group). In most cases (103 out of 132 reported) results are within $\pm 0{\cdot}2$ mg of $BiCl_3$. T. R. ANDREW

4739. **Behaviour of bismuth nitrate spots in inorganic paper chromatography.** E. C. Martin (School of Appl. Chem., Univ. of N.S.W., Sydney, Australia). *Anal. Chim. Acta*, 1960, **22** (3), 228–230 (in English).—The shapes and R_F values of the spots obtained with *n*-butanol - 2·5 *N* HSCN (7:2) as mobile phase depend on the anion present in the Bi soln. applied to the paper. This effect is particularly marked with NO_3^- and it is suggested that the NO_3^- travel ahead of the Bi spot and modify the cellulose in such a way as to increase the adsorption of Bi^{3+}. W. T. CARTER

4740. **Precipitation of basic bismuth formate from homogeneous solution and the determination of bismuth in presence of lead.** P. F. S. Cartwright (Dept. of Chem., Sir John Cass Coll., London). *Analyst*, 1960, **85**, 216–220.—The bismuth soln. is boiled at constant vol. with formic acid and urea and a few drops of bromocresol green indicator. Completion of the reaction is indicated by a change of colour in the hot soln. to bluish green. The ppt. is collected from the hot liquid in a tared porcelain crucible (porosity No. 4), washed with hot water, dried at 100° to 110° and cautiously ignited to Bi_2O_3. If lead is present in the sample the final ignited residue is tested for it. The trace that may be present should not be detectable except by a sensitive spot-test. A. O. JONES

4741. **Separation of bismuth from lead with (ethylenedinitrilo)tetra-acetic acid [EDTA]. Application to radiochemistry.** F. W. Lima and A. Abrão [Radiochemistry Div., Inst. de Energia Atôm., C.P. 11049 (Pinheiros) São Paulo, Brazil]. *Anal. Chem.*, 1960, **32** (4), 492–494.—A slight excess of EDTA is added to a soln. of Bi and Pb in HNO_3 and Bi is pptd. as the hydroxide by addition of NaOH soln. The degree of separation has been examined for mixtures of macro amounts ($\simeq$10 mg of each element) and for micro amounts ($\simeq$0·05 μC of ^{210}Pb in equilibrium with ^{210}Bi) in the presence and absence of major amounts of one of the ions.
T. R. ANDREW

4742. **Photometric determination of niobium [in alloys].** S. I. Barskaya. USSR Pat. 123,341 (22.10.59).—Niobium is determined in nickel, iron and titanium alloys by using as reagent Anthracene chrome violet (sodium 1-*o*-hydroxyphenylazo-2-naphthol-5-sulphonate) (**I**), which in 0·5 to 1·0 *N* HCl gives a red-violet colour with Nb, the intensity being proportional to the concn. of Nb. To determine Nb in titanium alloys, dissolve 0·5 g in 80 ml of HCl (sp. gr. 1·12), add a few drops of HNO_3 to clarify the soln., boil to remove oxides of N, cool, add 15 ml of 20% tartaric acid soln., make up to 250 ml, and to 2·5 or 5 ml add, with stirring, 20 ml of a soln. of **I** and 10 ml of HCl (1:1), set aside for 35 min., and measure the extinction with a green filter in a 50-mm cell. Determine the concn. of Nb from a calibration curve; 0·5 to 3·0% of Nb in an alloy can be determined with an error of $\pm$0·02%.
C. D. KOPKIN

4743. **Separation of niobium and tantalum together from titanium.** V. T. Athavale, V. P. Madhava Menon and C. Venkateswarlu (Anal. Div., Atomic Energy Estab., Trombay, India). *Analyst*, 1960, **85**, 208–211.—The mixed oxides of Nb, Ta and Ti are fused with $KHSO_4$ and the cooled melt is leached with a hot soln. of oxalic acid. Soln. of EDTA (disodium salt) and NH_4Cl are added, the diluted liquid is boiled, aq. NH_3 is added until the liquid is alkaline and, after further boiling and addition of filter-paper pulp, the mixture is set aside in a boiling-water bath for 20 min. The hot liquid is filtered and the ppt., after being washed with a hot soln. containing oxalic acid, EDTA and NH_4Cl and made alkaline with aq. NH_3, is ignited and weighed as R_2O_5.
A. O. JONES

4744. **Determination of niobium in the presence of tantalum after extraction with *iso*butyl methyl ketone.** P. Senise and L. Sant'Agostino (Dept. of Chem., Univ. of São Paulo, Brazil). *Anal. Chim. Acta*, 1960, **22** (3), 296–297 (in English).—Niobium can be separated from tantalum by extraction with *iso*butyl methyl ketone from 7·5 *N* HCl containing tartaric acid and H_2SO_4. *Procedure*—To the soln. (containing 5 to 15 μg of Nb, 10% of tartaric acid and 10% of H_2SO_4) (1 ml) add conc. HCl (2 ml) and extract with *iso*butyl methyl ketone (1 ml, 0·7 ml, 0·7 ml). To the combined extracts add phenylfluorone soln. (0·02% in 95 ml of ethanol and 5 ml of 23% H_2SO_4) (3 ml). Dilute to 10 ml with ethanol and measure the extinction at 502 mμ. Tantalum remains in the aq. phase but can be quant. extracted with *iso*butyl methyl ketone after the addition of 2% of HF.
W. T. CARTER

4745. **Spectrochemical determination of niobium and titanium in industrial tantalic acid.** K. Jordan and K. Picard. *Tech. Mitt. Krupp*, 1957, **15**, 203–207.—The method is suitable for the range 2 to 20% of Nb_2O_5 and 0·1 to 3% of TiO_2. The oxide mixtures, compressed with graphite to form tablets, were excited by a condensed low-voltage discharge. The analytical lines Nb 3098·47 A, Ti II 3017·19 and Ta 3098·0 were used. Calibration curves were established for the range indicated, and their reliability was proved on a series of test samples.
NUCL. SCI. ABSTR.

4746. **Separation of mixtures of niobium and zirconium by partition chromatography with alternation of phases.** S. Sekerskil and B. Kotlinskaya. *Atomnaya Energiya*, 1959, **7** (2), 160–162; *Ref. Zhur., Khim.*, 1960, (4), Abstr. No. 13,064.—The method is based on the sorption of Zr and Nb by tributyl phosphate (**I**) on "siliconised" silica gel, with subsequent elution with dil. HNO_3. The siliconised silica gel is prepared by treating "Hyflo Super Gel" silica gel with dimethylchlorosilane and drying at 100°; 0·5 g of the silica gel and 0·3 ml of **I** saturated with HNO_3 are placed in the column (diam. 0·5 cm) and the column is washed with dil. HNO_3 saturated with **I** to remove air. The test soln. (0·05 to 0·1 ml) containing radioactive isotopes of Zr and Nb is introduced. The sorbed components are separated by washing the column with 4·6 *M* HNO_3 saturated with **I**; pure Nb is first separated, and then Zr of radiochemical purity $>$98%. The separation is improved if 4·6 *M* HNO_3 containing 0·1 to 0·3% of H_2O_2 is used to elute Nb. To avoid a diffuse elution curve for Zr after the removal of Nb, it is recommended to wash the column with dil. HNO_3.
C. D. KOPKIN

4747. **Simple apparatus for the analysis of impurities in gases. Determinations of oxygen in an inert gas and of higher oxides of nitrogen in nitrous oxide.** G. Séris, P. Vernotte, —. Klein and A. M. Clavé. *Chim. Anal.*, 1960, **42** (4), 200–202.—An apparatus is described which permits O in inert gases to be determined with a precision of $\simeq$0·1 p.p.m. The apparatus is filled with the sample in the absence of air and the connecting tubing is freed from O desorbed from the walls by applying a vacuum. The gas is then treated with a soln. of anthraquinone-2-sulphonic acid in aq. NH_3, which has been stabilised with ammonium carbonate and reduced with zinc amalgam. Connected with the reaction vessel is a colorimetric cell in which the extinction of the reagent is read at 465 mμ before and after the reaction. A calibration curve must be prepared. For the determination of NO_2 and NO in nitrous oxide, the reagents are 1-naphthylamine and sulphanilic acid, both in acetic acid soln. Nitric oxide must first be oxidised to NO_2 with acid $KMnO_4$ soln., otherwise only NO_2 is determined. The extinctions are read at 526 mμ.
J. H. WATON

4748. **The determination of low oxygen content in high-melting metals by hot extraction with Feichtinger's apparatus. I. Iron bath method.** E. Lassner and E. Wölfel (Plansee Aktiengesellschaft, Reutte, Tirol, Austria). *Mikrochim. Acta*, 1960, (3), 394–404 (in German).—Results are presented for the determination of O (0·0001 to 0·02%) in molybdenum, tungsten and tantalum by the method of Feichtinger (*Anal. Abstr.*, 1956, **3**, 1923) after vacuum extraction in an iron bath at 1700°. A reproducibility of $\pm$0·0003% of O at 0·01% content and of $\pm$0·00007% at 0·0008% content is reported, and a mean relative error of $\pm$6·6% for O contents between 0·005 and 0·02% in molybdenum.
T. R. ANDREW

4749. **Absolute assay of sulphur-35 by internal gas counting.** W. F. Merritt and R. C. Hawkings (Atomic Energy of Canada Ltd., Chalk River, Ont.). *Anal. Chem.*, 1960, **32** (3), 308–310.—The sulphur to be assayed is converted into SO_2 by conversion into $BaSO_4$, and ignition with red phosphorus in an atmosphere of O. The SO_2 is mixed with methane into avoid the errors involved in measuring low pressures, and is then counted in an internal gas proportional counter. (*Cf.* Merritt *et al.*, *Anal. Abstr.*, 1960, **7**, 4750.) K. A. PROCTOR

4750. **The absolute counting of sulphur-35.** J. S. Merritt, J. G. V. Taylor, W. F. Merritt and P. J. Campion (Atomic Energy of Canada Ltd., Chalk River, Ont.). *Anal. Chem.*, 1960, **32** (3), 310–313.—A comparative study has been made of the methods of differential gas counting as SO_2, $4\pi\beta$-counting, and a tracer method, for determining the absolute disintegration rate of soln. containing ^{35}S.
K. A. PROCTOR

4751. **Improved method for the determination of small amounts of sulphate.** P. G. Quatermain and A. G. Hill (The British Drug Houses Ltd., Poole, Dorset, England). *Analyst*, 1960, **85**, 211–215.—The reagent is prepared by passing CO_2 over a boiling soln. of titanium in H_3PO_4. The sample is added to the cooled reagent, which is again heated in an all-glass apparatus, the stream of CO_2 being maintained to carry the H_2S formed by reduction into an absorber containing NaOH soln. Diphenylthiocarbazone indicator is added and the liquid is titrated with 0·001 *M* mercuric acetate until the colour changes from yellow to pink. Nitrates, Br^- and compounds containing oxidising anions interfere, $BaSO_4$ requires a longer reaction period, and with silver compounds weighing $>0·5$ g recovery is incomplete. Metals in a easily reduced high-valency state (even Cu^{II}) interfere by oxidising the titanous compound. Mercuric chloride also interferes. It is possible to determine down to 10 μg of SO_4^{2-} with an accuracy within ± 10 μg.
A. O. JONES

4752. **Modification for washing the benzidine sulphate precipitate in the determination of sulphate.** I. P. T. Häkkinen (Dept. of Physiol., Univ. Turku, Finland). *Nature*, 1960, **186**, 232.—After pptn. by the method of Kent and Whitehouse (*Anal. Abstr.*, 1956, **3**, 195) the following method of washing the ppt. is advocated. Transfer the contents of the pptn. tube to a 10-ml centrifuge tube tapering to a sharp point. Add 1 drop of an aq. suspension of $BaSO_4$, free from excess of Ba^{2+} and SO_4^{2-}, and centrifuge at 3000 r.p.m. for 5 min., then add 2 more drops of suspension and centrifuge for 15 to 20 min. Remove the supernatant liquid and dry the mouth of the tube with cellulose tissue. Add 9 ml of ethanol - acetone (1:1), break up the ppt. with a stiff steel wire and centrifuge for 5 min. Add 2 drops of the $BaSO_4$ suspension and centrifuge for 10 min. Decant off the upper layer, add 9 ml of ethanol - acetone and centrifuge for 10 min. Remove the supernatant liquid, add 3 ml of *N* HCl to dissolve the benzidine sulphate, breaking up the ppt. as before. After 30 min. add 2 ml of H_2O and centrifuge. Transfer the soln. to another tube for diazotisation by the method of Kent and Whitehouse.
H. F. W. KIRKPATRICK

4753. **Selenium and tellurium content of stony meteorites by neutron activation.** U. Schindewolf (Dept. Chemistry, Univ. of Michigan, Ann Arbor, U.S.A.). *Geochim. et Cosmoch. Acta*, 1960, **19** (2), 134–138.—Powdered meteorite samples are irradiated with neutron monitors in a heavy-water reactor, the irradiation lasting for 1 week before the analysis for Se or 12 hr. before analysis for Te. The Se is determined by neutron capture of ^{74}Se, the capture product being 128-day ^{75}Se which is easily detected and identified by three intense γ-rays; Te is determined from the β-activity of the 9·4-hr. ^{127}Te formed by neutron capture on ^{126}Te. Details are given for the chemical separation of Se and Te from the remainder of the sample, and from each other with a Dowex-1 anion-exchange column; this procedure can give a separation factor of Se from Te of $>10^4$.
R. A. HOWIE

4754. **The co-precipitation of impurities in the precipitation of tellurium with sulphur dioxide from hydrochloric acid solution.** H. Bode and E. Hettwer (Anorg.-chem. Inst., Tech. Hochschule, Hannover, Germany). *Z. anal. Chem.*, 1960, **173** (4), 285–300 (in German).—The effects of Cu, Cd, Hg, Tl, Sn, Pb, Sb, Bi, Mo, Ru, Rh, Pd, Os, Ir and Pt on the pptn. of Te were examined with acid concn. from 0·1 to 7 *N* at room temperature and at $\simeq 100°$. In general the minimum contamination was experienced by pptn. at 100° in 5 *N* HCl with SO_2 under pressure. Under these conditions Pd and Pt are quantitatively pptd. with Te; Hg, Ru, Rh, Os, Ir and Pb are partially pptd., but an effective separation can usually be achieved by re-pptn. under suitable conditions.
W. T. CARTER

4755. **Adsorption of tellurium(IV), iodide and iodate on anion-exchange resins.** E. Kleemann and G. Herrmann (Anorg.-chem. Inst., Univ., Mainz, Germany). *J. Chromatography*, 1960, **3** (3), 275–277 (in German).—The partition coeff. for the adsorption of Te^{4+}, I^- and IO_3^- from 2 to 10 *N* HCl on the anion-exchange resin Dowex 1-X10 are reported and discussed. There is evidence for partial reduction of IO_3^- to I^-. After adsorption from 4 to 8 *N* HCl, Te^{4+} can be effectively eluted with a few column-vol. of *N* HCl, but when other elements are present it is preferable to reduce Te^{4+} on the column to elementary Te (with 4 to 6 *N* HCl containing SO_2) and, after elution of the other elements with lower concn. of HCl, to re-oxidise the Te with 8 *N* HCl and HNO_3 before the elution with *N* HCl. Elution of IO_3^- with 0·01 *N* HCl after adsorption from conc. HCl containing SO_2 is possible, but the yield is low and often variable. The elution of I^- with warm 6 to 8 *N* HCl - SO_2 is also unsatisfactory, relatively large column-vol. of eluent being required.
W. J. BAKER

4756. **Volumetric determination of molybdenum. Reduction of molybdate ions in a silver reductor.** H. Grubitsch, K. Halvorsen and G. Schindler (Inst. für anorg.-chem. Tech. u. anal. Chem., Tech. Hochschule, Graz, Austria). *Z. anal. Chem.*, 1960, **173** (5), 414–420.—Molybdate ions in 2 *N* HCl are reduced to Mo^V at 75° in a silver reductor; the silver should be prepared by reducing $AgNO_3$ soln. with pure zinc, since traces of Cu catalyse the air oxidation of Mo^V. For a fairly rapid titration with $Ce(SO_4)_2$, with ferroin as indicator, the reduced soln. should be made 4 *N* in HCl; only traces of W may be present. For >5 mg of Mo, results are comparable with those obtained potentiometrically. For 1 to 5 mg of Mo, titration with 0·01 *N* $Ce(SO_4)_2$ gives more rapid and reproducible results. When $K_2Cr_2O_7$ soln. is used as titrant, with diphenylamine as indicator, negative errors of $\simeq 1\%$ are obtained; back-titration of the excess of $K_2Cr_2O_7$ with $FeSO_4$

soln. does not improve the results. By reducing Mo in 6 *N* HCl at 75° in the absence of air, Mo^{III} is quant. obtained. P. D. PARR-RICHARD

4757. **Oxidimetric methods for the volumetric determination of molybdenum(V). II. Titration with potassium dichromate, with diphenylbenzidine and N-phenylanthranilic acid as indicators. A study in redox indicator mechanisms.** M. Suryanarayana and G. Gopala Rao (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1960, **173** (5), 353–358 (in English).—In the titration of Mo^{V} with $K_2Cr_2O_7$, with diphenylbenzidine (**I**) as indicator, a fast reaction between **I** and $K_2Cr_2O_7$, induced by that between Mo^{V} and $K_2Cr_2O_7$, occurs in 4 to 5 *N* HCl. The oxidation is further catalysed, and the retarding effect of Mo^{VI} reduced, by the addition of conc. H_3PO_4. *Procedure*—To 5 to 15 ml of a 0·05 *N* soln. of Mo^{V} add 8 *N* HCl (30 ml) and conc. H_3PO_4 (3 ml) and dilute to 50 ml. Titrate with 0·05 *N* $K_2Cr_2O_7$ to a blue-violet end-point, with 0·25 ml of **I** soln. (0·1%) as indicator. If N-phenylanthranilic acid (**II**) is used as indicator, the slow reaction between oxidised **II** and Mo^{V} is catalysed by $VOSO_4$. To a known vol. of test soln. add 10 ml of 20 *N* H_2SO_4, 1 ml of conc. H_3PO_4, 1 to 2 ml of 0·05 *N* $VOSO_4$ and a few drops of **II** soln. (0·1%). Titrate with standard $K_2Cr_2O_7$ soln. to a pink end-point. P. D. PARR-RICHARD

4758. **Chemical analysis of calcined molybdenum trioxide.** S. Král (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1960, **15** (3), 215–217.—*Procedure*—After fusion of the sample (2 g) with Na_2O_2 and dissolution of the melt in water, Mo is determined in the filtrate as $PbMoO_4$, Cr by titration with $KMnO_4$ soln., V potentiometrically with $FeSO_4$ soln. and Al gravimetrically as Al_2O_3 (or $AlPO_4$ in samples containing >0·1% of P_2O_5). A second sample (5 g) is dissolved in aqua regia; Fe and Ti are pptd. as hydroxides, and Fe is determined by the Zimmermann-Reinhart method and Ti colorimetrically with H_2O_2. In the filtrate Ca is pptd. as oxalate and Mg is determined as $Mg_2P_2O_7$. Procedures are also given for the determination of the following elements, with a fresh sample for each—Si gravimetrically as SiO_2; P gravimetrically or volumetrically after pptn. with ammonium molybdate soln.; Cu + Ni polarographically; Sn polarographically; As volumetrically with iodine or $KBrO_3$ soln. after distillation as $AsCl_3$; Mn by the Proctor-Smith method; sulphide S either by combustion in a stream of O and determination of the SO_2 produced (for >0·1% of S) or by dissolution in HCl and determination of the liberated H_2S (for >0·1% of S); total S gravimetrically as $BaSO_4$; C volumetrically by combustion in a stream of O at 1100°; and Pb as $PbCrO_4$ after separation as $PbSO_4$. J. ZÝKA

4759. **The extraction of uranium.** V. Pfeifer and F. Hecht (Anal. Inst., Univ., Vienna). *Mikrochim. Acta*, 1960, (3), 378–389 (in German).—The extraction of U by tributyl phosphate and the back-extraction of U from the organic phase by soln. of complexing organic acids has been studied. After a preliminary extraction with benzoin α-oxime in $CHCl_3$ to remove Mo and W, the U is extracted from nitrate soln. with tributyl phosphate (50 ml in 250 ml of *cyclo*hexane), the *cyclo*hexane extract is shaken with *N* oxalic acid and the oxalic acid soln. is evaporated to dryness. The residue is evaporated to dryness with HCl (1 ml) and HNO_3 (1 ml), then dissolved in 10 ml of 0·01 *N* HNO_3 and the U is determined polarographically. The method is designed for >5 μg of U, and results obtained on a range of materials are in close agreement with those obtained by other methods.

T. R. ANDREW

4760. **Photometric determination of uranium with arsenazo.** V. I. Kuznetsov and I. V. Nikol'skaya (Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (3), 266–269.—Arsenazo gives a blue complex with U^{VI} and a bluish-violet complex with U^{IV}. The sensitivities of the reactions are similar, but the complex with U^{IV} forms at a lower pH. The colour of the U^{IV} complex in pure soln. remains unchanged for 1 hr., but the stability is reduced in the presence of Mo, V, Cu and other cations. At pH 1·5 to 1·8 the max. absorption occurs at 555 mμ, the reagent itself showing practically no absorption here and having a max. at 500 mμ. Selectivity can be increased by co-pptn. of the SCN^- complex with crystal violet in the presence of EDTA (disodium salt). To determine U in minerals, the sample (0·3 to 1·0 g, containing <0·003% of U) is ignited at 500° to 550° to destroy organic material, then moistened with water and treated with 10 ml of HF and 6 ml of $HClO_4$, followed by evaporation to dryness. Treatment with $HClO_4$ and evaporation is carried out twice more. The residue is dissolved in 2 to 3 ml of conc. HCl and the somewhat diluted soln. is heated almost to boiling after the addition of 5 mg of NH_4NO_3; aq. NH_3 free from CO_3^{2-} is added to precipitate hydroxides, which are then collected and washed with hot water containing aq. NH_3 and NH_4NO_3. The ppt. is dissolved in 10 to 20 ml of 2 *N* HCl and the soln. is treated with 20 ml of 5% EDTA (disodium salt) soln. and 5 ml of 40% NH_4SCN soln., then diluted to 250 ml and treated with aq. NH_3 to give a pH of 5 (universal indicator paper) followed by 2·5 ml of HCl (1:1). The well-shaken soln. is then treated dropwise with 25 ml of a saturated aq. soln. of crystal violet. After 1 hr. the ppt. is collected and washed five times with a soln. containing 8 ml of HCl, 4 ml of 40% NH_4SCN soln. and 5 ml of saturated crystal violet soln. in 1 litre. The ppt. is ignited at 500° to 600° and then heated with 4 to 5 ml of HCl. The insoluble matter is filtered off and washed with hot water containing HCl, and the soln. is treated with 0·8 ml of 10% KI soln. (to reduce U^{VI} to U^{IV}) and evaporated to dryness. The residue is dissolved in 10 ml of 0·1 *N* HCl and the soln. is treated dropwise with 0·002% $Na_2S_2O_3$ soln. to destroy the liberated iodine and then with 2 ml of 0·05% arsenazo soln. The soln. is diluted to 25 ml with 2% hydroxyammonium chloride soln. and the extinction is measured with a red filter. G. S. SMITH

4761. **Ultra-violet spectrophotometric determination of uranium.** A. H. A. Heyn and Gurupada Banerjee (Boston Univ.). *U.S. Atomic Energy Comm.*, Rep. NYO-7568, Nov., 1959. 25 pp.—A method was developed which is based on the u.v. absorption of the complex of U^{VI} with tri-(2-ethylhexyl)phosphine oxide (**I**). The complex is formed by extracting U^{VI} from an aq. 6 *M* $NaNO_3$ soln. in the pH range 2·5 to 3·0 with 0·1 *M* **I** soln. in an inert diluent, *cyclo*hexane. This extraction also separates the U from interfering ions. The reliable range for aq. samples is 0·0025 to 0·1 mg of U per ml. The standard deviation is <1% for both 0·05 mg of U per ml of the organic phase for 1-cm cells and 0·005 mg per ml for 5-cm cells. Extraction of U from 7 *M* HNO_3 with 0·1 *M* **I**, followed by stripping with Na_2CO_3 soln., was successfully utilised to

develop a method for the separation of U from a 10,000-fold excess of Bi. NUCL. SCI. ABSTR.

4762. **Rapid procedure for the spectrophotometric determination of uranium.** F. Vogliotti (Sicedison, Porto Marghera, Italy). *Energia Nucleare*, 1960, **7** (3), 169–175 (in English).—Details are given of a method for the analysis of ores that depends on the extraction of the U by tributyl phosphate - benzene (1:1) from a soln. containing KSCN, $Ca(NO_3)_2$ and EDTA at a pH between 1·3 and 1·8. The organic phase is washed with an acetate buffer soln. containing KSCN, EDTA and thioglycollic acid to remove co-extracted elements. The extinction of the organic phase is measured at 421 mμ and the content of U is derived from a standard curve. The respective amounts (50 to 250 mg) of 50 elements that do not interfere with the determination of 1·25 mg of U_3O_8 are tabulated. G. J. HUNTER

4763. **Determination of the alpha-activity due to uranium in aqueous sludges.** (U.K.A.E.A. Production Group, Operations Branch, Capenhurst). U.K.A.E.A. Rep. PG Report 120 (CA), 1960, 7 pp.—Uranium is leached from the dried sludge (1 g) with 8 *M* HNO_3 and purified by extraction into ethyl ether. After evaporation of the ether the U is mounted on a platinum tray, ignited, and then counted in an α-scintillation counter. The limit of detection is 5 disintegrations per min. per g of dried sludge. G. J. HUNTER

4764. **Separation and determination of uranium and thorium with 3-acetyl-4-hydroxycoumarin.** A. N. Bhat and D. Jain (Dept. of Chem., Univ. Delhi, India). *Talanta*, 1960, **4** (1), 13–17 (in English).—The complex of U^{VI} with 3-acetyl-4-hydroxycoumarin (**I**) is quant. pptd. from aq. ethanol in the pH range 1·5 to 4·5, but that of Th with **I** is sol. in ethanol and is pptd. only after removal of the ethanol. This enables U^{VI} (> 5·5 mg) to be determined and separated from Th (> 5-fold excess). Recoveries exceed 99·5%. No complex is formed by **I** with Ce^{III} or La and amounts > 10 times that of the U do not interfere. *Procedure*—To the aq. soln. of the nitrates of U^{VI} and Th add an equal vol. of ethanol (for a ratio of U_3O_8 to $ThO_2 > 1:2$, add twice the vol.). Warm the soln. and add 2% ethanolic **I** soln., with stirring. Cool, collect the ppt., wash with hot aq. ethanol (1:1) (200 ml), dry and ignite to U_3O_8. Evaporate the filtrate to remove ethanol and collect the ppt. appearing on cooling. Wash with water, dry, and ignite to ThO_2. J. P. STERN

4765. **Sensitive analytical method for carbon in uranium.** W. G. Smiley (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LA-1733, May, 1954. Decl. Mar., 1960. 28 pp.—The capillary-trap method for the determination of carbon in metals was modified by using a manometer in which the gas is compressed to a small vol., giving a linear scale and sensitivity of 0·1 μg of C per mm. Samples from pure uranium buttons gave standard deviations ranging from 1·4 to 3·2 p.p.m. Varying the sample size, in the range from 100 to 250 mg, did not affect the results significantly. The time required for an analysis was about 13 to 14 min. NUCL. SCI. ABSTR.

4766. **Square-wave polarography of plutonium.** K. Koyama (Hanford Laboratories Operation, General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 523–524.—At concn. $< 10^{-5}$ *M*, Pu can be easily determined in HCl or HNO_3 soln. The derivative wave-heights are proportional to concn., and half-wave reduction potentials agree with accepted values. The method is more sensitive than conventional polarography, and is unaffected by agitation of the sample or by irreversibly reducible materials, such as oxygen. K. A. PROCTOR

4767. **Determination of fluorine and impurities (hydrogen fluoride, carbon dioxide, oxygen and inert residue) in technical fluorine.** V. B. Aleskovskil and G. P. Tsÿplyatnikov. USSR Pat. 123,752 (9.11.59).—The gas is treated with solid NaCl, forming NaF; this absorbs HF to give $NaHF_2$, which is titrated with alkali; the other impurities are determined by suitable absorption processes. In an example, 12 g of powdered NaCl, previously ignited at 600° for 2 hr., is heated in a 400 to 900-ml stainless-steel cylindrical reactor for 50 min. at 340° and > 1 torr, then cooled. The reactor is filled with the sample of gas and sealed, shaken for 20 min. till completely cool, then connected to a liquid manometer containing a fluorinated oil (sp. gr. 1·85) and the pressure and temperature are measured. The gas in the reactor is displaced with dry N and analysed as indicated above. The residual $NaHF_2$ (0·5 to 2 g) is weighed into a beaker containing 2 ml of 10% KI soln. to reduce any Cl present, the soln. is diluted with 20 to 25 ml of water, and 0·1 *N* $Na_2S_2O_3$ is added so as just to reduce the iodine. The soln. is then titrated with 0·3 to 0·5 *N* NaOH to phenolphthalein or potentiometrically. C. D. KOPKIN

4768. **Rapid determination of fluorine in phosphate rocks.** L. Shapiro (U.S. Geological Survey, Washington, D.C.). *Anal. Chem.*, 1960, **32** (4), 569–570.—The enhancement by Ca of the intensity of the alizarin-3-sulphonate - Al colour is diminished in the presence of F^-, but is unaffected by PO_4^{3-}. *Procedure*—Transfer 50 mg of sample, 50 mg of standard rock containing 3 to 4% of F, and 25 mg of standard rock to three 100-ml flasks. Add HNO_3 (3 *N*) (10 ml) to each flask, and use a further portion of acid for a blank. Dilute to volume and mix. Pass 20 ml through an ion-exchange column (Amberlite IR-120, H^+ form) and wash the resin with 30 ml of H_2O. Combine the percolate and washings in 100-ml flasks. Prepare two aliquots of the acid blank. To all the soln. except one acid blank add a soln. of Al (8·75 μg of Al per ml) (15 ml). To all the soln. add $Ca(NO_3)_2$ soln. (14%) (2 ml), buffer soln. (70 g of Na acetate, 30 ml of acetic acid and 470 ml of H_2O) (10 ml) and set aside for 10 min.; then add 5 ml of Alizarin red S soln. (0·1%), dilute to volume, mix, set aside for 1 hr. and record the extinction at 475 mμ, with the blank soln. without Al as reference. A calibration curve is constructed from the blank with Al, and the two standard soln., from which the F^- content of the sample can be determined. T. R. ANDREW

4769. **Voltammetric, potentiometric and amperometric studies with a rotated aluminium wire electrode. IV. A comparison of the Baker and Morrison cell with the RAlE [determination of fluoride].** I. M. Kolthoff and C. J. Sambucetti (School of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (3), 253–260 (in English).—If in the amperometric determination of F^- the RAlE (rotated aluminium electrode) is used with a reference electrode of 5% cadmium amalgam in equilibrium with *M* $CdSO_4$ and satd. KCl, a linear relationship is obtained between the

current flow in the short-circuited cell and F^- concn. in 0·2 *M* acetic acid in the range 10^{-5} to 10^{-4} *M*. The RAIE is satisfactory in the presence of O, but the Baker and Morrison electrode (*Anal. Abstr.*, 1955, **2**, 3350) is not; Cl^- and ClO_4^- do not interfere up to a concn. of 0·01 *M*. The standard addition method can be used in the presence of air, but the removal of O is recommended. W. T. CARTER

4770. **Determination of oxides in fluoride salts by high-temperature fluorination with potassium bromotetrafluoride.** G. Goldberg, A. S. Meyer, jun., and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 314–317. —Amounts of O from 0·02 to 10 mg are determined by heating the sample for 2 hr. at 450° with an excess of $KBrF_4$. The liberated O is measured manometrically. Recoveries of >98% are found for pure metal oxides, with a coeff. of variation of <5%; when fluoride samples are analysed, the precision is ≃8%. The method has also been applied successfully to other halide salts, and is useful for the determination of O in metals and alloys where fusion methods fail. Inert gases and N interfere. J. H. WATON

4771. **Mercury(I) titrations with Variamine blue as redox indicator. Determination of chloride, bromide and mercurous ions.** Z. Gregorowicz and J. Stoch (Inst. f. anorg. Chem., Schlesischen Techn. Hochschule, Gliwice, Poland). *Z. anal. Chem.*, 1960, **173** (5), 383–388.—The function of Variamine blue (C.I. Azoic Diazo Component 35) (**I**) as a redox indicator in the titration of Cl^- or Br^- with $Hg_2(NO_3)_2$ at pH 2 to 6 is discussed. The oxidation of **I** by Hg_2^{2+} is strongly accelerated by NH_4NO_3; nitrates of Ca, Na or K are not so effective and large amounts of Hg_2Cl_2 retard the process; Hg_2^{2+} in excess gradually attack the violet oxidation product of **I**, more rapidly in hot soln. *Procedure*—Add 1 g of solid NH_4NO_3 to 10 ml of Cl^- soln. and titrate slowly with 0·1 *N* $Hg_2(NO_3)_2$, adding 0·5 ml of a 0·1% soln. of **I** near the end-point. At 50°, the titre is the same as that obtained by other methods; 0·005 *N* to 0·5 *N* soln. of Cl^- and Br^- can be titrated successfully; Hg_2^{2+} can be determined by adding an excess of standard Cl^- soln. and back-titrating with standard $Hg_2(NO_3)_2$ soln. P. D. PARR-RICHARD

4772. **Determination of chlorate and perchlorate in presence of each other.** A. de Sousa (Fac. of Sci., Univ. of Lisbon, Portugal). *Chemist Analyst*, 1960, **49** (1), 18.—Ignite a portion of the sample in a platinum dish with 12 times its wt. of NH_4Cl for 1 to 2 hr. at below the fusion-point. Precipitate the Cl^- (formed by reduction of both chlorate and perchlorate) as AgCl. Reduce the chlorate only, by heating a second portion of the sample (>200 mg of ClO_3^-) with 10% $FeSO_4$ soln. (50 ml) at boiling-point for 15 min. with constant stirring. Cool and add HNO_3 to re-dissolve any basic iron salts present. Precipitate Cl^- as AgCl. Determine the Cl^- in each ppt. as follows. After washing the ppt. thoroughly, first with 0·1% $AgNO_3$ soln. then with 1% HNO_3, cover the filter crucibles with 0·1 *M* $KNi(CN)_4$ [titrate 0·1 mole of $NiSO_4$ in dil. aq. NH_3 (500 ml) with *M* KCN in the presence of murexide to a colour change from yellow to purple, then dilute to 1 litre]. Warm to assist dissolution, dilute to 500 ml, add murexide soln. and titrate with 0·1 *M* EDTA (disodium salt). G. S. ROBERTS

4773. **Determination of iodides in the presence of bromides and chlorides by means of radioactive iodine.** M. D. Morachevskaya and B. V. Ptitsŷn (Leningrad Technol. Inst. of the Food Industry). *Zavod Lab.*, 1960, **26** (3), 269–271.—The soln. is mixed with a known vol. of a soln. of iodine of known concn. in KI soln. of known concn. and also with a soln. containing radioactive iodine as NaI. After 5 min., which is long enough for isotopic exchange, the iodine is extracted with CCl_4, and the activities of the extract and aq. soln. are measured after suitable dilution. G. S. SMITH

4774. **Polarographic determination of manganese.** R. F. Sympson and V. E. Caldwell (Dept. of Chem., Ohio Univ., Athens, U.S.A.). *Chemist Analyst*, 1960, **49** (1), 19–20.—A yellow complex, containing Mn^{III}, is produced when a strongly alkaline soln. of the chelating agent, ethylenediaminedi-(*o*-hydroxyphenylacetic acid) is added to a soln. of Mn^{II} in the presence of O. The complex is readily reducible at the dropping-mercury electrode. Bivalent Co interferes, but not low concn. of Pb, Al, Zn, Cd, Cu^{II}, Ni, Fe^{III}, Cr^{III}, Mg, Ca, Sr or Ba. G. S. ROBERTS

4775. **Determination of metallic iron impurity in manganese ores.** N. S. Tkachenko and P. I. Davidenko. USSR Pat. 123,949 (20.11.59).—Iron is extracted from manganese ores, materials containing free MnO_2 or other oxidising agents such as V_2O_5 and As_2O_5, and iron powders, by heating with a soln. of $HgCl_2$ in methanol in the presence of sodium salicylate, and determined in the filtrate colorimetrically as the sulphosalicylic acid complex at pH 4·5 to 7·0 (acetate buffer soln.). C. D. KOPKIN

4776. **Separation and identification of manganese, technetium, rhenium, ruthenium and molybdenum on the ultra-micro scale.** F. Jasim, R. J. Magee and C. L. Wilson (Dept. of Chem., Queen's Univ., Belfast, N. Ireland). *Talanta*, 1960, **4** (1), 17–24 (in English).—A scheme for the qual. separation of Tc from the other Group-VII elements and from Mo and Ru, which are likely preparative contaminants, is presented. *Procedure*—Add to the test soln. (50 to 100 mμ) ≃ 0·5 vol. of 10% NaOH, soln., boil, and centrifuge. Separate the liquid (containing Mo, Re and Tc) from the residue, acidify the soln. with 2 *N* HCl, reduce to small vol. and add 2% 8-hydroxyquinoline soln. in 4 *N* acetic acid; heat, and centrifuge. An orange-yellow ppt. indicates Mo. To the supernatant liquid add satd. aq. potassium xanthate soln. and then CCl_4 or $CHCl_3$, and centrifuge. A purple colour in the organic phase indicates Tc. Test the aq. phase for Re with dimethylglyoxime and an excess of $SnCl_2$; a red-orange colour confirms the presence of Re. The original residue may contain Mn and Ru. Dissolve it in the min. vol. of 4 *N* HCl, heat, and add ammonium sulphide soln. Boil the soln. (which should now be acid) for 3 min., cool, and centrifuge. Test the supernatant liquid for Mn. Dissolve the ppt. in the min. vol. of hot 2 *N* HNO_3 and test for Ru with KOCN; a blue colour, completely extractable by *iso*butyl methyl ketone, confirms the presence of Ru. Semi-quant. estimation of the ions present is possible by measuring the vol. of ppt. formed, and a scheme for treating mixtures of Re, Tc and Mo is presented that involves pptn. of Mo as the 8-hydroxyquinoline complex and the separation of Tc^{IV} from Re by pptn. with aq. NH_3 in the presence of an iron salt as carrier. The Tc^{IV} is then oxidised to Tc^{VII} and pptd. as tetraphenylarsonium pertechnetate, the Re remaining in soln. being then determined as Re_2S_7. J. P. STERN

4777. **Analytical investigations of pyrolusites. Rapid method for the determination of the composition of $MnO_1 + x$ products.** G. Gattow and H.-G. Wendlandt (Anorg.-chem. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1960, **174** (1), 15–23 (in German).—After iodimetric determination of the oxidising power of the sample, the sample soln. is reduced with hydroxyammonium chloride soln., a 5% excess of 0·01 *M* EDTA is added, and the soln. is made just alkaline with NaOH soln. and adjusted to pH 10 by addition of aq. NH_3 - NH_4Cl buffer soln. [composition not given] before titrating with a standard soln. of Zn, with Eriochrome black T as indicator. The procedure is applicable to samples of from 10 to 30 mg, and results (for $1 + x$) are within 0·2% of those obtained by macro-methods (*e.g.*, $MnO_{1·917}$ as against $MnO_{1·914}$ by macro-techniques). T. R. ANDREW

4778. **Determination of rhenium by a differential spectrometric method.** T. M. Malyutina, B. M. Dobkina and Yu. A. Chernikhov (State Sci. Res. and Development Inst. of the Rare Metals Industry). *Zavod. Lab.*, 1960, **26** (3), 259–263.—The thiourea method of Ryabchikov and Lazarev (*Anal. Abstr.*, 1956, **3**, 1357) is applied to the determination of high concn. of Re by differential spectrometry. For calibration, various amounts from 2 to 2·7 ml of a standard soln. of $KReO_4$ containing 1 mg of Re per ml are each treated with 10 ml of conc. HCl, 10 ml of 5% thiourea soln., and 2 ml of a 20% soln. of $SnCl_2$ in conc. HCl, and then diluted to 50 ml. After 35 to 40 min. the extinction of each soln. is measured at 390 mμ in a 1-cm cell, with reference to a null soln. containing 2 mg of Re. The mean factor, concn. difference/extinction, is calculated. Alternatively, a calibration curve relating extinction to concn. can be drawn. For samples of titanium - rhenium alloy containing $\geq$30% of Re, 50 to 100 mg is dissolved in the cold in 10 ml of HCl (1 : 1) and 4 ml of HF, and the soln. is boiled with 4 g of H_3BO_3, 40 to 60 ml of water and 1 to 2 drops of 3% H_2O_2 soln. until it is nearly colourless, water being added to maintain the vol. at between 50 and 80 ml. The cooled soln. is diluted to 100 ml, and a 10-ml aliquot in a 50-ml flask is treated with the reagents as described for the calibration. With alloys containing between 30 and 40% of Re, the sample (50 to 100 ml) in a nickel or silver crucible is fused at 400° to 500° with some $NaNO_3$ and 2 g of NaOH to give a transparent melt, which is then dissolved in 20 to 40 ml of hot water. The soln. is treated with 20 to 30 ml of conc. HCl and diluted to 100 ml. A 10-ml aliquot is then treated as described above. G. S. SMITH

4779. **Rapid extraction of iron(III) with 2-thenoyltrifluoroacetone. Direct colorimetric determination in the organic phase.** S. M. Khopkar and Anil K. De (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **22** (3), 223–228 (in English).—The Fe^{III} complex can be quant. extracted with benzene at pH 2·0. The extinction of the benzene soln. is measured at 460 mμ and Beer's law is obeyed over the range 1 to 10 μg of Fe per ml; U, Ce, Th, Zr, Cu, Ag, Ni, Mn, Bi, Al, phosphate, citrate and tartrate interfere. For six determinations of 200 μg of Fe the coeff. of variation was ±1·14%. W. T. CARTER

4780. **The volumetric determination of small amounts of iron. II.** B. Salovius, V. P. Hirsjärvi and M. Uosukainen (State Agric. Lab., Helsinki, Finland). *Mikrochim. Acta*, 1960, (3), 357–365 (in German).—Copper (1 mg), Co (1 mg), Mn (1 mg) and Ca (80 mg) do not interfere in the titration of 0·5 to 4 mg of Fe^{II} with 0·005 *N* $K_2Cr_2O_7$. Phosphoric acid is tolerated up to a concn. of 0·65 *M*. Some observations on indicator corrections are made. N-Methyldiphenylamine-*p*-sulphonic acid (sodium salt) is recommended as a better indicator than Na diphenylaminesulphonate. (For Part I see *Anal. Abstr.*, 1960, **7**, 4267.) T. R. ANDREW

4781. **Complexometric estimation of ferric iron.** Balwant Singh, S. S. Sahota and M. S. Mankotia (Dept. of Chem., Punjab Univ., Hoshiapur, India). *Z. anal. Chem.*, 1960, **173** (4), 275–278 (in English).—Ferric iron can be titrated with EDTA (disodium salt) soln., with 0·2 *N* aq. KSCN - 0·2 *N* ethanolic *p*-anisidine (1 : 1) as indicator. Barium, Ca, Mg, Hg, Mn, Sr, Cr and Zn do not interfere. W. T. CARTER

4782. **Spectrophotometric determination of iron(III) with *o*-dianisidine.** C. Vassiliades and G. Manoussakis (Univ., Thessalonika, Greece). *Bull. Soc. Chim. France*, 1960, (2), 390–393.—The formation of a complex between Fe^{III} and *o*-dianisidine is investigated; the reaction is very sensitive and Fe^{II} does not interfere. Under suitable conditions a red colour is formed with max. absorption at 450 mμ, and this colour is most intense at pH 2·5 to 3·0. The colour develops slowly at room temp. (<18°) and absorption readings must be made between 40 and 50 min. after mixing. No solid complex could be isolated, but a study of the variation of colour by Job's method gives a max. at a ratio of Fe to dianisidine of 2 : 1. Beer's law is obeyed for Fe^{3+} concn. <0·001%. The colour is scarcely perceptible for 1 part of Fe in 8×10^7 parts of water. Gold and nitrites interefere in concn. equal to that of the Fe, and Ag^+, Pd^{2+}, Ru^{3+} and Pt^{4+} interfere in concn. twice that of Fe; tartrate, CrO_4^{2-}, $Cr_2O_7^{2-}$ and I^- interfere in high concn. A list of ions known not to interfere is given, and the application of this procedure to the determination of Fe in bauxite is described. E. J. H. BIRCH

4783. **Oxidation - reduction reactions on ion-exchange columns. Reduction of iron(III) ions on ion exchange - stannous columns.** L. Erdey, J. Inczédy and I. Markovits (Inst. Gen. Chem., Tech. Univ., Budapest, Hungary). *Talanta*, 1960, **4** (1), 25–32 (in English).—An ion-exchange resin is effectively converted into an electron-exchange resin by adsorption of a reducing or oxidising ion. This principle is adapted for the determination of Fe^{3+} on either a cation or an anion exchanger. Adsorption of Fe^{3+} on Wofatit KPS 200 or Lewatit S-100 (H^+ form), and subsequent passage through the resin of 2% aq. ascorbic acid (**I**) soln., produces Fe^{2+}. The excess of **I** is washed out with 0·01 *N* H_2SO_4 and the Fe^{2+} are then eluted with 4 *N* H_2SO_4 and titrated with $KMnO_4$. Quant. separation from PO_4^{3-} is possible but reducible ions behaving like Fe^{3+} (*e.g.*, vanadate) interfere. The accuracy on 1 to 2·5 millimoles of Fe is within ±0·15%. Alternatively, $SnCl_2$ (<2 equiv.) is adsorbed on Lewatit-MN resin at 40° to 50° and Fe^{3+} in 3 *N* HCl are then added. Slow elution with 3 *N* HCl is continued until the eluate gives no red colour with H_2O_2 - KSCN. The eluate is cooled and titrated with $Ce(SO_4)_2$ soln., with ferroin as indicator, or with $KMnO_4$ after the addition of Zimmermann - Reinhardt soln. The accuracy on 0·24 to 1·2 and

on 0·02 to 1·0 millimole of Fe^{3+} is within ±0·24 to ±0·04% and ±0·1%, respectively.
J. P. STERN

4784. **Photometric determination of iron in bronzes not containing tin.** L. Ya. Polyak. USSR Pat. 120,677 (19.6.59).—Diantipyrinylmethane is used as reagent, giving with Fe^{3+} in weakly acid medium a red - brown coloration of intensity proportional to the concn. of Fe. The colour is stable. A 200-fold excess of Cu does not interfere; Al, Mg, Zn, Cd, Mn, Ni, Co and Cr do not interfere. A blue or green filter is recommended. C. D. KOPKIN

4785. **Precipitation of crystalline iron(III) oxide from homogeneous solution.** E. R. Nightingale, jun., and R. F. Benck (Dept. of Chem., Univ. of Nebraska, Lincoln, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 566–567.—Urea (5 to 10 g) is added to 100 ml of 0·001 *M* Fe^{III} soln. containing 0·01 *M* HCl and 0·002 to 0·02 *M* NN-di-(2-hydroxyethyl)glycine, and the soln. is brought rapidly to boiling-point. After 1 to 10 min. a granular ppt. forms, and the soln. is immediately removed from the source of heat and filtered. The ppt. may be washed without peptisation. The ppt. has been identified as β-FeO.OH. Precipitation is only 90 to 98% efficient unless boiling is prolonged, which tends to peptise the ppt. T. R. ANDREW

4786. **Determination of ferrocyanides in the presence of ferricyanides, cyanides and thiocyanates. II. Volumetry.** S. Arribas Jimeno and B. Losa Martín (Univ., Oviedo, Spain). *Inf. Quím. Anal.*, 1960, **14** (2), 31–33.—The determinations were carried out on the ppt. obtained by treating the ferrocyanide soln. with aq. ammonium molybdate soln. in the presence of NH_4Cl, with either the yellow ppt. obtained on the addition of a Na acetate - acetic acid buffer or the reddish - brown ppt. obtained in strong acid medium (HCl). The ppt. was either (*i*) dissolved in aq. $NaHCO_3$ soln., treated with an excess of iodine soln. and the excess determined by titration or (*ii*) dissolved in acid medium, treated with an oxidising agent [$Ce(SO_4)_2$, $KMnO_4$ or $K_2Cr_2O_7$] and the excess determined volumetrically. Equal accuracy was obtained by either method, in the presence of SCN^-, CN^- or $[Fe(CN)_6]^{3-}$.
L. A. O'NEILL

4787. **Determination of a mixture of cementite, carbon, iron and iron oxides. Analysis of ferro-cokes.** F. Marion (Lab. de Mét., Fac. des Sci., Lille, France). *Bull. Soc. Chim. France*, 1960, (2), 393–394.—The selective dissolution of Fe from cementite and iron oxides at various temp. is investigated and a method for the determination of cementite, carbon, iron and iron oxides in a sample is developed. *Procedure*—The finely powdered sample is analysed for total C by the method of N. F. AFNOR AO6-301. The cementite is determined by selective decarbonation with H - water vapour (*Anal. Abstr.*, 1959, **6**, 1740). Cementite and metallic Fe are dissolved at the b.p. with $(NH_4)_2Ag(SCN)_4$ soln. at pH 5 and the Fe is determined according to Marion and Aubry (*Anal. Abstr.*, 1960, **7**, 2729). Correction for any iron oxides dissolved is made by treating two samples for 20 and 40 min., respectively, and extrapolating the Fe content to zero time. The oxides are determined in the residue from the Fe and cementite determination after elimination of Ag as bromoargentate with KBr - $KBrO_3$. The method is less precise when used for mixtures poor in Fe but rich in cementite and FeO. E. J. H. BIRCH

4788. **Determination of oxygen, hydrogen and nitrogen in steel by the vacuum fusion method.** M. Kaše and M. Mandl (Výzkumný Ústav Hutnictví Železa, Prague). *Hutn. Listy*, 1960, **15** (3), 195–200.—The apparatus is described. The sample is heated in a graphite crucible at 1650° for 30 min. with induced current from a high-frequency generator. The gas pressure is measured, then the gases are passed over copper oxide at 550° for 5 min. to convert CO into CO_2 and H to H_2O. Water vapour is condensed by a mixture of acetone and solid CO_2, the resulting difference in pressure giving the H content of the mixture. Carbon dioxide is then condensed in a vessel surrounded by liquid air, and the gas pressure is again measured after 5 min. The results are examined statistically. P. G.

4789. **Semi-micro determination of chromium in steel containing not more than 7% of chromium in the absence of vanadium.** J. Hanák. *Hutn. Listy*, 1960, **15** (3), 217–218.—Dissolve the sample (0·1 g) by gentle heating in 10 ml of a mixture of 20 ml of H_2SO_4 (d = 1·84), 25 ml of H_2PO_4 (d = 1·7) and 145 ml of H_2O; oxidise with conc. HNO_3 (5 drops) and remove nitrogen oxides by boiling. Cool the soln., dilute with H_2O (20 ml), add $AgNO_3$ soln. (1%) (1 ml) and $KMnO_4$ soln. (1%) (4 ml) and boil for 3 min. Add HCl (1:1) (1 ml), dilute with hot H_2SO_4 (1:40) (20 ml) and boil for 6 min. Cool, add N-phenylanthranilic acid soln. (0·2 g + 0·2 g of Na_2CO_3 in 100 ml of H_2O) (3 drops) and titrate till green with a soln. of $(NH_4)_2SO_4.FeSO_4$ [dissolve 5 g in 500 ml of H_2O, add 50 ml of H_2SO_4 (d = 1·84), cool and dilute with H_2O to 1 litre]. J. ZÝKA

4790. **Potassium cobaltinitrite as a precipitation form for cobalt using radio-cobalt tracer.** D. Salyer and T. R. Sweet (Dept. of Chem., McPherson Chem. Lab., Ohio State Univ., Columbus, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 548–550.—By means of a tracer technique the effects of the several variables on the gravimetric determination of Co as $K_3Co(NO_2)_6$ have been investigated. At low temp. (20°) and high concn. of KNO_2 (20 to 30%, w/v), quant. pptn. of up to 0·5 g of Co is obtained in 30 min. Increase in temp., decrease in KNO_2 concn. or increase in concn. of Co increased the time necessary for complete pptn. T. R. ANDREW

4791. **Spectrophotometric determination of noble metals with tin(II) in bromide solutions.** F. Pantani and G. Piccardi (Inst. of Anal. Chem., Univ. of Florence, Italy). *Anal. Chim. Acta*, 1960, **22** (3), 231–236 (in English).—The colours given by Pt, Rh, Pd, Ir and Au with $SnBr_2$ are all suitable for quant. colorimetry. They are all stable and obey Beer's law and, with the exception of the Au complex, can be extracted into *iso*amyl alcohol. Certain mixtures can be analysed by a choice of reaction conditions. Gold can be separated from the platinum metals by extracting as $HAuBr_4$ with ethyl ether or *iso*amyl alcohol. Iridium does not react with $SnBr_2$ at room temp. and mixtures with Pt, Rh or Pd can be analysed by treatment at room temp. followed by extraction with *iso*amyl alcohol; Ir can then be determined in the aq. phase by heating with $SnBr_2$. Platinum and Rh can be separated from Pd by extracting the Pd complex of 1-nitroso-2-naphthol with *iso*amyl alcohol. Mixtures of Rh and Pd can be analysed by a differential spectrophotometric procedure which gives recoveries accurate to ±3% for amounts of 100 to 250 μg.
W. T. CARTER

4792. **The isolation of platinum metals from partially refined concentrates.** H. Zachariasen and F. E. Beamish (Univ. of Toronto, Canada). *Talanta*, 1960, **4** (1), 44–50.—Methods applicable both to large scale work and to analysis for dissolving partly refined concentrates and for isolating platinum metals, Ag and Au therefrom are described. After reduction with H (removal of H_2S and reduction of oxides), the residue is leached with HNO_3 (1:4) and Ag is pptd. from the soln. with HCl. The residue (insol. in HNO_3) is treated with aqua regia and hydrated SnO_2 is pptd. Material insol. in aqua regia is mixed with Na_2CO_3 and sintered at 710° for 3 hr. or at 780° to 790° for 2 hr. The solid is extracted with HCl, leaving SiO_2 as residue and this soln. is used for the separation of the precious metals. Ruthenium is separated by evaporation with H_2SO_4 and distillation with $NaBrO_3$. The Ru is collected in HCl (1:1) containing 3% of H_2O_2 and determined gravimetrically with thionalide. The Au and Pt are separated from Pd, Rh, Ir and base metals by the Gilchrist bromate hydrolysis procedure (*J. Res. Nat. Bur. Stand.*, 1934, **12**, 291); Au is then pptd. with quinol and Pt with thiophenol. Any Te is removed from the Pt by heating in H at 750° for 30 min. The Pd is separated with dimethylglyoxime and Rh is separated from Ir by reduction with copper powder in *N* HCl; the Rh - Cu residue is dissolved in acid and the metal chlorides are separated by ion exchange; Rh is then determined by pptn. with thiobarbituric acid. The Ir and Cu in soln. are separated by ion exchange and the Ir is determined by hydrolysis with $NaBrO_3$. Results for a 1-g sample agree well with standard values.
J. P. STERN

4793. **Determination of sub-microgram quantities of ruthenium by catalysis of the cerium(IV) - arsenic(III) reaction.** C. Surasiti and E. B. Sandell (Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (3), 261–269.—By measuring the time required for the extinction of a soln. containing Ce^{IV} and As^{III} to decrease to a specified value it is possible to determine quantities of Ru (0·005 to 0·1 μg) too small to be determined colorimetrically. The method is not affected by the presence of Fe, Ni, Pt, Pd, Rh and Ir, but Os interferes seriously and must be removed by the extraction of OsO_4 with CCl_4 or by volatilisation from an H_2SO_4 soln. containing H_2O_2. *Procedure*—Remove HNO_3 from the soln. by evaporation with conc. HCl, and halides by adding H_2SO_4 (1:1) (5 ml) and fuming for 1 hr. Dilute to 100 ml, add 30% H_2O_2 (1 to 2 ml) and evaporate to one-half the vol. Repeat this procedure twice. Cool, add 0·5 g of Ag_2O and set aside for 10 min. Extract with CCl_4 (3 × 10 ml) and shake the combined extracts with 2 *M* H_2SO_4 (5 ml) containing a little Ag_2O. Discard the aq. phase. Shake the CCl_4 mechanically for 2 hr. with 2 *M* H_2SO_4 (10 ml) containing Na_2SO_3 (3·2 mg) and discard the CCl_4. To a 2-ml aliquot of the aq. phase add ceric ammonium sulphate (0·16 *M* in 2 *M* H_2SO_4) (1 ml) and adjust the temp. to 25°. Mix as rapidly as possible with 0·16 *N* As_2O_3 (1 ml) at 25° and measure the time for the transmittance to reach 60% (against H_2O) at 488 mμ, with a 1-cm cell thermostatically controlled at 25°. Refer the result to a standard curve of Ru concn. *vs.* reciprocal of reaction time. For pure soln. the precision is ≃2%. In the presence of 100 μg of Os it is reduced to ≃10%. W. T. CARTER

4794. **Spectrophotometric determination of rhodium with NN′-bis-(3-dimethylaminopropyl)dithio-oxamide.** W. D. Jacobs (Dept. of Chem., Univ. of Georgia, Athens, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 514–516.—Tervalent Rh gives a yellow colour (absorption max. at 420 mμ) with NN′-bis-(3-dimethylaminopropyl)dithio-oxamide when heated for 1 hr. at 90° in 7·5 *M* HCl. The sensitivity of the reaction is 0·012 μg of Rh^{IV} per sq. cm. Details are given for the elimination of the interference due to other metals of the platinum group.
T. R. ANDREW

4795. **Separation of rhodium from iridium by copper powder.** G. G. Tertipis and F. E. Beamish (Univ. of Toronto, Ontario, Canada). *Anal. Chem.*, 1960, **32** (4), 486–489.—Rhodium is pptd. by heating the sample soln. (*N* in HCl) (20 to 30 ml) with 500 mg of freshly reduced copper powder at 91° to 93° for 1 hr. with regular gentle swirling at 1-min. intervals; a further 200 mg is added after 30 min. The ppt. is collected in a sintered-glass funnel and subsequently dissolved in aqua regia. The resulting soln. and the filtrate from the original pptn. of Rh are freed from Cu by passage through a cation-exchange column (Dowex 50X), and Rh and Ir are determined photometrically in the percolates. The separation is almost quantitative (10 to 14 μg of Rh is detected in 2 to 10 mg of iridium ppt., and 10 to 24 μg of Ir is detected in 2 to 10 mg of rhodium ppt. from approximately 1:1 mixtures). Recoveries of 0·05 to 10 mg of each element are > 99%.
T. R. ANDREW

4796. **Spectrophotometric study of NN′-bis-(3-dimethylaminopropyl)dithio-oxamide as a reagent for palladium.** W. D. Jacobs (Dept. of Chem., Univ. of Georgia, Athens, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 512–513.—In HCl soln. Pd^{II} reacts with NN′-bis-(3-dimethylaminopropyl)dithio-oxamide to give a yellow colour (absorption max. at 427 mμ). The extinction of the complex is constant and at its max. at HCl concn. of 3·4 *M* to 7 *M*. The sensitivity is 0·008 μg of Pd^{II} per sq. cm. The interference of 12 ions has been studied. T. R. ANDREW

4797. **New fire assay for osmium and ruthenium.** J. M. Kavanagh and F. E. Beamish (Univ. of Toronto, Ontario, Canada). *Anal. Chem.*, 1960, **32** (4), 490–491.—The improved fire assay procedure of Plummer and Beamish (*Anal. Chem.*, 1959, **31**, 1141) is shown to be applicable to the determination of Os and Ru. The lead button is dissolved in $HClO_4$, and Os and Ru are distilled off and determined with thionalide. Recoveries on known amounts of Os from 2 to 10 mg show a max. error of −0·08 mg (14 samples), while for Ru in the range 2 to 8 mg the max. error was +0·09 mg in the normal process (14 samples), rising to −0·18 mg in a determination in which air was passed through the distillate for 10 hr. T. R. ANDREW

4798. **Determination of trace elements in silicate rocks by a combined spectrochemical - anion-exchange technique.** R. R. Brooks, L. H. Ahrens and S. R. Taylor (Dept. of Physiology, University of Cape Town). *Geochim. et Cosmoch. Acta*, 1960, **18** (3–4), 162–175.—A further investigation is reported into methods combining anionic-exchange enrichment techniques with spectrographic analysis (*cf. Anal. Abstr.*, 1960, **7**, 162). Silver, Pb, Sn, Bi, Cd, Zn, Tl, Mo and In, which form chloro complexes in HCl, are adsorbed on IR-400 basic anion exchanger. After elution and evaporation the residues are analysed quant. by a d.c. arc method. Results for the determination of Cd, Zn, Bi, Tl and Sn in 19 rock samples are given. R. A. HOWIE

4799. **Infra-red determination of the kaolin-group minerals.** R. J. P. Lyon and W. M. Tuddenham (Geochem. Section, Dept. of Earth Sciences, Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Nature*, 1960, **185**, 835–836.—The ratio between the depths of the i.r. hydroxyl absorptions of halloysite, kaolinite and dickite gives the content of each in mixtures. Peaks at 2·70 μ (*A*) and 2·75 μ (*B*) are common to all three minerals. A peak depth ratio (*A*:*B*) of 1·2 to 1·5 is characteristic of kaolinite, one of 0·8 to 0·9 of halloysite and one of 0·6 to 0·8 of dickite. Spectra due to Si–O and Al–Si–O between 8·9 μ and 10·1 μ show a diagnostic pair of doublets. A doublet at 10·7 μ and 11·0 μ is typical of kaolinite and dickite; halloysite shows only a single peak at 11·0 μ. An inspection of the ratio *A*:*B* and the presence or absence of absorption at 10·7 μ enables the three minerals to be distinguished.

D. C. ARMSWORTH

4800. **Rapid determination of potassium chlorate and potassium dichromate in the mass used for match production.** Z. Marczenko and Z. Skorko-Trybuła (Katedra Chem. Anal., Politech., Warszawa). *Chem. Anal., Warsaw*, 1960, **5** (1), 71–77.—The sum of $KClO_3$ and $K_2Cr_2O_7$ is determined by adding an excess of 0·2 *N* $(NH_4)_2SO_4.FeSO_4.6H_2O$ and titrating with $KMnO_4$. Potassium dichromate is then determined separately by means of the colour of Cr^{VI} in sulphuric acid. Interference with the colour development may be caused by azo dyes present in the mass and these must be decomposed with ammonium persulphate.

M. MORAN

See also Abstracts—**4629**, Zinc acetate as a reagent. **4631**, Sulphonamide dyes as reagents. **4632**, Pyromellitein adsorption indicators for argentimetric titrations. **4633**, Benzidine derivatives as metallofluorescent indicators. **4634**, Complexometric fluorescent indicators. **4638**, Osmium tetroxide as oxidation catalyst in volumetric analysis. **4640**, Coulometric determination of Cu, Au, Hg and ferricyanide. **4900**, Determination of Ca and Mg. **4903**, Determination of Al. **4947**, Differential determination of hydroxylamine and hydroxamates. **5067**, Continuous gas titration analyser for F. **5118**, Gases in metals. **5122**, Cd, Ni and Zn in metals.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives, etc.

4801. **Determination of occluded solvent in organic compounds.** C. E. Childs and E. B. Henner (Res. Lab., Parke, Davis & Co., Detroit, Mich., U.S.A.). *Chemist Analyst*, 1960, **49** (1), 26.—The sample is heated in a stream of dry air and condensable material is collected in a cold trap. The condensate is analysed by gas - liquid chromatography.

G. S. ROBERTS

4802. **Liquid scintillation counting of tritiated organic compounds.** M. L. Whisman, B. H. Eccleston and F. E. Armstrong (Bartlesville Petroleum Res. Center, Bureau of Mines, U.S. Dept. of Interior, Okla.). *Anal. Chem.*, 1960, **32** (4), 484–486.—The effects of certain variables on the measurement of the radioactivity of tritiated organic compounds by liquid scintillation techniques have been studied, and the following routine procedure was developed. The scintillation soln. (15 ml) is measured into each of two phials and identical amounts of sample soln. are added to each, to give approx. 5000 to 10,000 counts per min. An internal standard (tritiated toluene, $2·2 \times 10^6$ disintegrations per min. per ml) is added to one phial in sufficient quantity to give 10 times the total count expected from the sample. After standing at −10° for 1 to 2 hr., each mixture is counted for 3 to 10 min., depending on the total radioactivity present. A background count on 15 ml of scintillation soln. is also obtained. The radioactivity is then calculated from an equation. By using the conditions described, the counting error is ±1·4% and coincidence losses are negligible if the count rate is below 300,000 c.p.m. The standard deviation of a single determination of a tritiated hydrocarbon is ±2%.

S. M. MARSH

4803. **The analytical chemistry of organometallics. Quantitative determination of organoalkalis.** A. F. Clifford and R. R. Olsen (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 544–546.—This new procedure involves the reaction of organoalkali compounds (*e.g.*, phenyl-lithium) with an excess of iodine. A known volume of organoalkali soln. is added with constant stirring and in an inert atmosphere (N) to a standardised (≃0·6 *N*) soln. of iodine in diethyl ether, containing at least 2 moles of iodine for every 1 mole of organoalkali expected. After stirring the mixture for 3 min., 25 ml of water, acidified to pH 5 with HCl, is added together with 3 g of KI. The unchanged iodine is then titrated with standard $Na_2S_2O_3$ soln., with starch as indicator. The method has been compared with the acid titration and carbonation methods. It is certainly more accurate than the former and probably more accurate than the latter, and is not subject to the obvious errors of the other methods. Other types of organometallic compound, *e.g.*, those containing Mg or Pb, may also be determined.

S. M. MARSH

4804. **Determination of halogens by fusion with potassium metal.** V. K. Bukina and M. Ya. Molzhes. *Dokl. Akad. Nauk UzSSR*, 1959, (2), 27–29; *Ref. Zhur., Khim.*, 1960, (4), Abstr. No. 13,143.—The titration of excess of $AgNO_3$ in the determination of halogens in organic substances by fusion with potassium metal (*cf.* Korshun *et al.*, *Anal. Abstr.*, 1955, **2**, 3074) is modified. Because of the low accuracy in determining the halogens by titration with 0·025 *N* NH_4SCN, it is proposed to titrate with 0·01 *N* KI in the presence of starch and iodine, which form the blue colour only in the presence of I^-, *i.e.*, after pptn. of Ag^+. The organic substance (15 to 20 mg) is fused with potassium in a steel micro-bomb, the melt is dissolved in water and made up to a known vol. To 20 ml of the soln. 5 or 6 drops of H_2O_2 are added to oxidise cyanides, excess of H_2O_2 is destroyed by boiling for 5 to 7 min., 1 ml of HNO_3 (sp. gr. 1·4) and 6 to 8 ml of 0·01 *N* $AgNO_3$ are added, the ppt. is filtered off, and the filtrate is titrated with 0·01 *N* KI in the presence of starch and iodine. The abs. error is about ±0·3%.

C. D. KOPKIN

4805. **Micro-determination of some elements in organic compounds after decomposition with potassium. I. Determination of halogens.** L. Mázor, L. Erdey and T. Meisel (Inst. f. allg. Chem., Tech. Univ., Budapest). *Mikrochim. Acta*, 1960, (3), 412–416 (in German).—The sample (8 to 10 mg) is weighed into a tube (100 mm × 8 mm) and covered with a layer (≃15 mm) of small glass beads. Potassium is added and heated to fusion, when it sinks through the beads and reacts with the sample. The cooled melt is extracted with water and boiled for 5 min. with 10 drops of H_2O_2 (30%) to "deactivate" any carbon formed during the reaction. The soln. is acidified with HNO_3 to phenolphthalein, and an acetate buffer (pH 3·6) is added before titration with $AgNO_3$ soln. (0·01 *N* or 0·002 *N*), with Variamine blue as indicator. The technique is not applicable to volatile compounds.

II. Determination of sulphur. L. Mázor, L. Erdey and T. Meisel. *Ibid.*, 1960, (3), 417–420.—After fusion of the sample as described in Part I, the cooled melt is extracted with methanol (1 ml) and transferred to a 250-ml flask with Na_2SO_3 (0·5 g), *N* NaOH (8 ml) and 100 ml of water. Aq. 3-aminophthalhydrazide (luminol) soln. (0·01%) (2 to 3 ml) is added and the soln. is titrated in darkness with 0·01 *N* $[Fe(CN)_6]^{3-}$ until the appearance of luminescence. T. R. Andrew

4806. **Micro-determination of chlorine (bromine) and sulphur in organic compounds in a single sample.** G. Giesselmann and I. Hagedorn (Chem. Lab. Univ., Freiburg/Brsg., Germany). *Mikrochim. Acta*, 1960, (3), 390–393 (in German).—After combustion of the sample in an O-filled flask according to Schöniger (*Anal. Abstr.*, 1955, **2**, 1816) the liberated SO_4^{2-} are titrated with $BaClO_4$ (*cf.* Wagner, *Anal. Abstr.*, 1957, **4**, 2996). Chloride or Br^- may now be titrated with $AgClO_4$ soln. in 80% *iso*propyl alcohol, with dichlorofluorescein as indicator. Results are within ±1% of theoretical values. T. R. Andrew

4807. **Simple, rapid automatic micro-Dumas apparatus for nitrogen determination.** G. M. Gustin (Celanese Corp. of America, Summit, N.J.). *Microchem. J.*, 1960, **4** (1), 43–54.—A completely automatic, compact and simply operated train is described; CO_2 is rapidly absorbed by magnetically stirred KOH soln. and the N is measured in a 5-ml calibrated syringe. One furnace containing CuO is operated at 850° to completely pyrolyse all types of organic material, and a second furnace containing copper and CuO is operated at 400° to 500° for the further treatment of the combustion and dissociation products. Samples of 1 to 10 mg, and 6 samples per hour, can be analysed. The coefficient of variation is 0·3% at the 10 to 30% level, and 0·01% of N can be determined. G. P. Cook

4808. **Comparison of the Kjeldahl and Dumas methods for the determination of nitrogen.** H. Hübsch and K. Nehring (Oskar Kellner Inst. für Tierernährung, Rostock, Germany). *Z. anal. Chem.*, 1960, **173** (4), 278–284 (in German).—The discrepancies in the nitrogen balances carried out on pigs and rats (*cf.* Nehring, *Biochem. Z.*, 1957, **328**, 549) cannot be explained by analytical error since both the Dumas and Kjeldahl methods give similar results. A modified Kjeldahl method in which 30% H_2O_2 is used gives results that agree closely with the normal Kjeldahl method for a large range of samples of animal origin. A considerable saving in time is possible, but care is necessary to avoid losses due to frothing. W. T. Carter

4809. **Micro-determination of sulphur in organic compounds utilising the Schöniger combustion.** A. Steyermark, E. A. Bass, C. C. Johnston and J. C. Dell (Hoffmann-La Roche Inc., Nutley, N.J., U.S.A.). *Microchem. J.*, 1960, **4** (1), 55–58.—Certain substances, particularly those containing –SH and sulphonamide groups, give low results when analysed by the Carius combustion method. When samples of this type are decomposed in the Schöniger flask the results are in agreement with theoretical values for S. G. P. Cook

4810. **Volumetric micro-determination of organic sulphur following the Schöniger combustion.** H. Soep and P. Demoen (Res. Lab. Dr. C. Janssen, Beerse, Belgium). *Microchem. J.*, 1960, **4** (1), 77–87.—Three methods for determining the SO_4^{2-} after combustion were compared. In the first, titration with $Ba(ClO_4)_2$ soln. was used, with thoron as indicator; in the second, $Ba(NO_3)_2$ soln. was used as titrant and Na alizarinsulphonate as indicator, and in the third, $Pb(NO_3)_2$ soln. and dithizone. The third method was the most satisfactory. The Schöniger method was extended to the determination of S in volatile compounds by using a simple capsule made of adhesive cellulose tape. G. P. Cook

4811. **De-sulphurisation as a method of identifying sulphur compounds.** C. J. Thompson, H. J. Coleman, C. C. Ward and H. T. Rall (Bartlesville Petroleum Res. Center, Bureau of Mines, U.S. Dept. of the Interior, Bartlesville, Okla.). *Anal. Chem.*, 1960, **32** (3), 424–430.—The lack of reference compounds and spectra makes the identification of many sulphur compounds isolated by micro-separation methods difficult. An apparatus and method are described for removing the S so as to obtain hydrocarbons for which reference material is available. The sample is passed in a stream of H over a catalyst of palladium (5%) on activated alumina at 150° to 200°. The product is condensed in a stainless-steel capillary, from which it can be removed by a drop of a suitable solvent for identification by gas-liquid chromatography. Known sulphur compounds (10) yielded the expected hydrocarbons. The sulphur compound cannot always be uniquely identified by this procedure, but other data may assist. The method can also be used for the identification of certain compounds containing O and N. Extremely small samples (< 0·0002 ml) can be handled. G. Burger

4812. **Determination of microgram quantities of sulphate in organic linkages.** G. Zdybek, D. S. McCann and A. J. Boyle (Dept. of Chem., Wayne State Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 558–560.—Chloric acid may be used for the digestion procedure before the turbidimetric determination of micro amounts of organic sulphate. Aliquots of sample soln. containing up to 300 μg of S are pipetted into test-tubes (25 mm × 150 mm). To each are added 10% $NaNO_3$ soln. (1 ml) and 25% chloric acid soln. (4 ml) and digestion is carried out to incipient dryness at 120° in an aluminium heating-block. After cooling the products, 1 ml of satd. ammonium carbonate soln. is added and the mixtures are again evaporated to dryness and cooled. De-ionised water (6 ml) is added to dissolve the salts and when the tubes have cooled to room

temp. conc. HNO_3 (0·03 ml) and ethanol - dipropylene glycol (9:11) (4 ml) are added, followed by 5 ml of $BaCl_2$ reagent (6 ml of 1·34 *M* $BaCl_2$ in de-ionised water diluted to 120 ml, and 80 ml of ethanol - dipropylene glycol soln. added). The mixtures are inverted 5 times, and transferred to 0·75-in. matched tubes for development of turbidity. After 25 to 30 min. the turbidity is measured at 355 mμ. The standard deviation for seven samples containing 100 μg of S is ±2·3 μg. Numerous samples may be run simultaneously with a minimum of manipulation. S. M. MARSH

4813. **Investigation of the determination of phosphorus in organic compounds.** W. J. Kirsten and M. E. Carlsson (Res. Lab., Pharmacia Ltd., Uppsala, Sweden). *Microchem. J.*, 1960, **4** (1), 3–31.—A number of procedures for the mineralisation and spectrophotometric determination of P in org. compounds were studied. For mineralisation, the open-tube wet-combustion method is the fastest, simplest and most convenient for samples containing down to a few μg of P. The sealed-tube method permits the analysis of both volatile compounds and aq. soln. but takes longer, and large samples cannot be analysed. The flask combustion method works satisfactorily but there is a slight tendency towards low results. The spectrophotometric methods investigated were the yellow molybdophosphoric acid and the molybdenum blue procedures. Measurement of the yellow molybdophosphoric acid colour at 400 or 430 mμ is the fastest, simplest and most accurate of the colorimetric methods tested; 460 mμ is preferable if a lower sensitivity is desired. Amyl acetate is an excellent extractant for molybdophosphoric acid and separates it completely from molybdosilicic acid and most other interfering substances. Molybdenum blue methods should be used when high sensitivities are required.

G. P. COOK

4814. **The micro-determination of alkoxyl groups.** B. Buděšínský and J. Körbl (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Mikrochim. Acta*, 1960, (3), 369–377 (in German).—A study of the effect of formic acid concn. on the titration of liberated alkyl iodide in Zeisel's method has led to an improvement in precision by the use of a constant amount of formic acid (1·5 ml of 2·1% soln.). Sodium antimonyl tartrate soln. (10%) is recommended as a scrubbing soln. to remove iodine and HI vapour. A readily cleaned all-glass apparatus is described. A determination (on a 3-mg sample) may be made in about 30 min. T. R. ANDREW

4815. **Micro-determination of alkoxyl groups by a new combustion method.** Minoru Fukuda (Pharm. Fac., Univ. Osaka, Japan). *Mikrochim. Acta*, 1960, (3), 448–459 (in English).—The alkyl iodide, formed after treatment of the sample (3 mg) in the usual manner with P and HI, is led in a stream of air through a furnace tube packed with a platinum catalyst at 750°. The liberated iodine is absorbed by silver gauze at 200° to 350° and the increase in weight permits direct calculation of total alkoxyl groups, while if the CO_2 liberated is subsequently absorbed in KOH and weighed, the nature of the alkoxyl group may be deduced. For removing iodine and HI from the alkyl iodide stream, a solid reagent is recommended; this is prepared by fusing together NaOH (60 g), H_2O (3 g), soda lime (20 g) and NiO ("small amount") and grinding the cooled product to 1 to 2-mm size.

T. R. ANDREW

4816. **Infra-red absorption frequencies of the *tert.*-butoxy group.** H. A. Ory (Plastics Div., Monsanto Chemical Co., Texas City, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 509–511.—The i.r. absorption spectra of 17 compounds have been used to determine the absorption regions of the *tert.*-butoxy group. These lie between 720 and 1200 cm^{-1}. Molecular configurations influence the spectra exhibited by the various compounds.

K. A. PROCTOR

4817. **Chromatographic analysis of gas mixtures containing hydrogen, nitrogen and methane.** N. S. Torocheshnikov and V. A. Seminova (Moscow Chem.-Technol. Inst.). *Zhur. Prikl. Khim.*, 1960, **33** (3), 597–602.—Apparatus is described for the chromatographic separation of H, N and CH_4 in natural water and in industrial gases. The gas mixtures are adsorbed on a column of activated carbon (AG-2 or SKT) and then desorbed by passing CO_2 through the column. Errors are >1%. A. BURWOOD-SMITH

4818. **Determination of hydrocarbon oxidation products. Reverse isotope dilution analysis.** W. H. Clingman, jun., and H. H. Hammen (American Oil Co., Texas City, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 323–325.—The application of the reverse isotope dilution method to the determination of known components of the products of radiation-induced oxidation of propane is described. The propane was labelled with ^{14}C and oxidised in a sealed ampoule with air and ZnO. The products were either gaseous or were adsorbed on the catalyst. The ampoule was broken inside a sealed vessel containing 15 ml each of up to 3 of the compounds to be determined and set aside for 16 hr. If more than one component was added they were separated by distillation. A derivative of each added component was prepared, purified, and assayed for ^{14}C by the method of Sechrist and Hammen (*Ind. Eng. Chem.*, 1958, **50**, 341). G. BURGER

4819. **Characterisation of alkyl halides by use of ethylenethiourea.** R. N. Boyd and M. Meadow (Dept. of Chem., New York Univ., N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 551–554.—Alkyl halides can be satisfactorily identified by formation of their 2-alkylthio-4:5-dihydroglyoxalinium salts and the corresponding free bases and picrates of these bases. The 4:5-dihydroglyoxalinium salts are obtained by heating the halide under reflux with ethylenethiourea in *n*-propanol for 6 hr. The corresponding free bases and their picrates are prepared in the usual way. The melting-points, analyses and equivalent weights are tabulated for all three types of derivative for a comprehensive series of alkyl halides and dihalides. S. M. MARSH

4820. **Characterisation of alkyl halides.** P. M. G. Bavin (Chem. Dept., Hull Univ., England). *Anal. Chem.*, 1960, **32** (4), 554–556.—The methyl fluorene-9-carboxylate anion reacts rapidly with many alkyl halides to give the corresponding methyl 9-alkylfluorene-9-carboxylates, most of which are easily crystallised. The alkyl halide is added to a soln. of methyl fluorene-9-carboxylate (prep. described) in dry methanol containing Na methoxide, and is either left to stand or warmed on a steam bath according to the reactivity of the halide. The derivatives are obtained by diluting with water, extracting with dichloromethane and recrystallising from methanol or hexane. The size of the alkyl group may be determined by saponification and

determination of the equiv. wt. of the 9-alkylfluorene-9-carboxylic acid obtained. The melting-points of the derivatives from a wide range of alkyl halides, including some tertiary halides, polymethylene dihalides and hydroxyalkyl halides, are tabulated.
S. M. MARSH

4821. **Separate and total determination of normal, secondary and tertiary butyl alcohols.** Ya. E. Shmulyakovskiĭ. USSR Pat. 124,197 (20.11.59).—The alcohols are converted into the corresponding nitrites as follows. A mixture of 10 ml of heptane, 10 ml of the aq. test soln., 0·5 ml of 5 *N* HCl and 0·5 ml of 25% $NaNO_2$ soln. is shaken in a separating-funnel for 5 min., the layers are allowed to separate, and the aq. layer is removed. Excess of HNO_2 in the funnel is neutralised by shaking with 10 ml of 0·5 *N* ammonium carbonate for 5 min., and the aq. layer is again removed. The extinction of the resulting soln. of the mixed butyl nitrites in heptane is measured. The individual components are determined from their u.v. absorption spectra (main maximum for *iso*butyl nitrite 356 mμ, for *tert.*-butyl nitrite 382 mμ).
C. D. KOPKIN

4822. **Detection of polyhydric compounds and their carboxylate esters with potassium periodatocuprate.** T. G. Bonner (Royal Holloway Coll., Egham, Surrey, England). *Chem. & Ind.*, 1960, (13), 345.—Potassium periodatocuprate (**I**) is a sensitive reagent for detecting easily oxidisable substances such as sugars, polyhydric compounds, phenols and their ester derivatives. When applied to paper, **I** gives a brownish background against which the oxidised compound appears as a white spot. As the background colour soon disappears, a permanent record is made of the spot by marking or by spraying with a rosaniline base soln. within 1 min. of its development.
G. P. COOK

4823. **Radiometric determination of carboxyl groups in cellulose by means of calcium-45.** J. Hostomský, J. Tölgyessy and V. Kriváň (Dept. Radiochem., Inst. Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (4), 290–294.—*Procedure*—To the sample (0·5 to 1 g, previously de-cationised by a 30-min. treatment with 2 *N* HCl, then washed and dried) add a soln. of Ca acetate (10 ml) containing ^{45}Ca (relative specific activity $\simeq$10,000 counts per min. per ml) and mix. After $<$12 hr. transfer 0·5 ml of the supernatant liquid to a small dish of thin aluminium and spread the liquid in a thin layer on the bottom of the dish. Evaporate under an i.r. lamp and measure the radioactivity with a Geiger - Müller tube. Carry out a blank and calculate the Ca-bound carboxyl-group content from the decrease in activity.
J. ZÝKA

4824. **Spot test for formaldehyde and formaldehyde-liberating compounds.** E. Jungreis (Dept. of Inorg. and Anal. Chem., Hebrew Univ., Jerusalem, Israel). *Chemist Analyst*, 1960, **49** (1), 14.—Formaldehyde condenses with hydroxylamine to produce formaldoxime, which forms an orange compound with an alkaline soln. of a Mn^{II} salt. The test is specific for formaldehyde (5 μg) and compounds such as hexamine (15 μg) which release formaldehyde under pyrohydrolytic conditions.
G. S. ROBERTS

4825. **Rapid method for semi-quantitative determination of volatile aldehydes, ketones and acids. Flash exchange gas chromatography.** J. W. Ralls (Western Reg. Res. Lab., Albany, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 332–336.—The procedure described is especially suitable for the determination, to within 20%, of the volatile flavouring constituents of vegetables in concn. of a few p.p.m. in water. Aldehydes and ketones are isolated as the 2:4-dinitrophenylhydrazones and C_1 to C_{10} aliphatic monocarboxylic acids as the potassium salts. The 2:4-dinitrophenylhydrazones are heated to 250° for 10 sec. with an excess of α-oxoglutaric acid in a capillary connected to the inlet of a gas-chromatography column. The parent compounds are liberated and pass into the column. The potassium salts are heated to 300° in the same manner with an equal wt. of potassium ethyl sulphate; the ethyl esters distil into the column.
G. BURGER

4826. **Critical solution temperatures of some systems with dibasic organic acids.** F. Gölles (Inst. f. Pharmakogn., Univ. Graz, Austria). *Mikrochim. Acta*, 1960, (3), 429–447 (in German).—Values are presented for the critical temp. of the systems water, *n*-butanol or *sec.*-butyl alcohol, and oxalic, malonic or succinic acid, at several concn., for use in the micro-determination of these acids in aq. soln. by the method of Fischer (*cf. Anal. Abstr.*, 1955, **2**, 3183; 1958, **5**, 2770).
T. R. ANDREW

4827. **Cerate oxidimetry. V. Oxidation of mixtures of citric and oxalic acids.** N. N. Sharma and R. C. Mehrotra (Chem. Lab., Univ. of Allahabad and Gorakhpur, India). *Z. anal. Chem.*, 1960, **174** (1), 35–38 (in English).—When a mixture of citric and oxalic acids is heated under reflux with excess of standard $Ce(SO_4)_2$ soln., in the presence of dil. H_2SO_4, citric acid is oxidised to formic acid while oxalic acid is completely decomposed to CO_2 and H_2O. If Cr^{3+} and conc. H_2SO_4 are added to the soln. and the heating under reflux is continued, the formic acid is also completely oxidised by the excess of Ce^{IV}. The quantity of Ce^{IV} reduced in the presence and absence of Cr^{3+} permits calculation of the initial content of citric and oxalic acids.
T. R. ANDREW

4828. **Determination of methyl 1-methylbutylidenecyanoacetate by polarography.** H. Marciszewski (Inst. Farm., Warszawa). *Chem. Anal., Warsaw*, 1960, **5** (1), 119–123.—The method is used as a means of controlling the reduction of methyl 1-methylbutylidenecyanoacetate to methyl 1-methylbutylcyanoacetate. The calibration curve was determined over the range 20 to 100 μg per ml. As a supporting electrolyte 0·1 *N* KCl was used, and $E_{\frac{1}{2}} = -1{\cdot}72$ V *vs.* the S.C.E. The polarographic results were compared with those obtained by measurement of the refractive index.
W. B. MIASKOWSKI

4829. **Assay and characterisation of amines by means of 1-fluoro-2:4-dinitrobenzene.** D. T. Dubin (Nat. Inst. of Arthritis and Metabol. Diseases, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1960, **235** (3), 783–786.—A simple, sensitive, colorimetric assay is described for aliphatic amines and amino acids. After the reaction of the amine with the fluorodinitrobenzene, dioxan is added to the aq. reaction mixture to effect dissolution of the coloured condensation product and the extinction is then determined spectrophotometrically. Dimethylformamide can also be used instead of dioxan. The ratio of the extinctions at 350 mμ and 390 mμ

is a useful value for differentiating between primary and secondary amines. For primary amines the ratio of the extinction at 350 mμ to that at 390 mμ is approx. 0·5 to 0·8; for secondary amines and amino acids it is approx. 2·1 to 2·4. The method will determine 10 to 150 mμ-equiv. of amino group.
J. N. ASHLEY

4830. **The detection of organic [mercapto] compounds.** L. Rosenthaler (Seftigenstrasse 40, Bern). *Pharm. Acta Helv.*, 1960, **35** (3), 81–86 (in German).—Precipitation and colour reactions of 3-mercaptopropane-1:2-diol, thioglycollic acid, dithiomalic acid, thiophenol, thiobenzoic acid, thiosalicylic acid, thiourea and thiobarbituric acid are listed. They generally differ from those of the corresponding compounds with O in place of S. A. R. ROGERS

4831. **Mercurimetric titration of thiourea and its derivatives in the presence of *p*-dimethylaminobenzylidinerhodanine as indicator.** M. Wroński (Inst. Chem. Technol., Univ. Łódź, Poland). *Z. anal. Chem.*, 1960, **174** (1), 3–5 (in German).—Thiourea, thiosemicarbazide and substituted thioureas may be titrated, in aqueous or alcoholic soln. 0·1 to 0·2 *N* in $HClO_4$, with tris(acetoxymercuri)aniline soln. after addition of 0·5 ml of *p*-dimethylaminobenzylidinerhodanine soln. (0·05%). Halides, SO_3^{2-} and $S_2O_3^{2-}$ must be absent. A procedure is given for the determination of thiourea - sulphide mixtures. The reagent is prepared as follows. Ethanolic aniline soln. (10%) (20 ml) is boiled gently for 90 min. with 125 ml of *N* mercuric acetate in 0·2 *N* acetic acid, 500 ml of H_2O is added with 5 ml of 80% acetic acid, insoluble by-products are filtered off and the soln. is diluted to 1 litre (≃0·05 *N*). Recoveries on 2 to 150-mg samples were within 1%, while for 0·2 mg of thiourea the result was 3% high.
T. R. ANDREW

4832. **The infra-red spectrum of dimethyl sulphone.** Kuniaki Fujimori (Nippon Mining Co., Funakawa Refinery, Oga-shi, Akita). *Bull. Chem. Soc. Japan*, 1959, **32** (12), 1374–1376 (in English).—Previously determined force and vibration constants for the methylsulphonate ion (*Ibid.*, 1959, **32**, 621) have been used to calculate the normal vibrations of dimethyl sulphone, and the results are compared with experimental results. Calculated values for S-O stretching are 1252 and 1345 cm^{-1}, while the observed spectrum gives peaks at 1130, 1290 and 1315 cm^{-1}. For S-CH_3 stretching, observed values are 695 and 761 cm^{-1}, while the calculated values are 741 and 795 cm^{-1}. The discrepancies between these values is attributed to the very high value assigned to the S-O stretching force constants.
T. R. ANDREW

4833. **The vibrational spectra of organic *iso*thiocyanates.** N. S. Ham and J. B. Willis (Div. of Chem. Phys., C.S.I.R.O., Chem. Res. Lab., Melbourne, Australia). *Spectrochim. Acta*, 1960, **16** (3), 279–301.—Analysis of the Raman and i.r. spectra of a series of aliphatic and aromatic *iso*thiocyanates shows two frequencies for each compound which are characteristic of an aliphatic or aromatic NCS group. The complex structure of the band near 2100 cm^{-1}, which is peculiar to the *iso*thiocyanates, is interpreted. P. T. BEALE

4834. **Colorimetric determination of dialkyl phosphites using cacotheline.** T. D. Smith (Chem. Dept., Royal Coll. of Sci. and Technol., Glasgow, Scotland). *Anal. Chim. Acta*, 1960, **22** (3), 249–252 (in English).—Alkyl phosphites produce an immediate red coloration with cacotheline in alkaline soln. The reaction requires three moles of alkyl phosphite to one of cacotheline. *Procedure*—Into a 50-ml flask place *N* Na_2CO_3 (5 ml) and 0·01 *M* cacotheline (10 ml). Add the sample soln. (≃5 mg of alkyl phosphite), dilute to volume and measure the extinction at 560 mμ. For diethyl phosphite Beer's law is obeyed over the range 0·2 to 5·0 mg and the colour is stable for at least 3 hr.
W. T. CARTER

4835. **Spot-test detection of esters of non-carboxylic acids.** F. Feigl and V. Anger (Lab. de Producao Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1960, **49** (1), 13–14.—The detection of the alkyl esters of phosphorothioic, phosphorodithioic, phosphonic, arylsulphonic, sulphuric and boric acids commonly found in wetting agents and insecticides is described. *Procedure*—Mix the sample with $Na_2S_2O_3.5H_2O$ and heat slowly to 180°. When most of the water of crystallisation has evaporated hold a strip of Congo red paper, moistened with 3% H_2O_2, close to the melt. A blue colour, due to the evolution of SO_3, indicates a positive reaction. Other compounds that yield SO_3 under the same conditions include primary alkyl halides, free carboxylic acids and sulphonic acids, and salts of amines weaker than ammonia.
G. S. ROBERTS

4836. **Determination of poly(methylhydrogensiloxane) in poly(dimethylsiloxane) fluids.** P. J. Launer and M. E. Grenoble (Gen. Electric Co., Waterford, N.Y.). *Anal. Chem.*, 1960, **32** (3), 441.—Infra-red data are given.

4837. **Quantitative de-alkylation of alkylboron compounds by carboxylic acids.** J. Crighton, A. K. Holliday, A. G. Massey and N. R. Thompson (Univ. Liverpool, England). *Chem. & Ind.*, 1960, (13), 347.—Heating a soln. of trimethylboron in ethyl ether at 40° with undried propionic acid in a sealed tube effected the fission of only one methyl group as methane, but the dried acid produced 2 mol. of methane. Similar results were obtained with dried acetic and trifluoroacetic acids in the absence of ether. By heating at 130° to 140°, 96% of the total available methane was obtained with propionic acid, and tributylboron gave a 100% yield with acetic acid. These and other results suggest that initial co-ordination of the carboxylic acid followed by intramolecular elimination of the alkane must occur rather than a direct proton attack.
G. P. COOK

4838. **Vapour-phase separation of methyl- or ethyl-mercury compounds and metallic mercury.** Y. Kimura and V. L. Miller (Western Washington Exp. Sta., Washington State Univ., Puyallup, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 420–424.—The mixed vapour of mercury alkyls and mercury is passed successively through a carbonate - phosphate soln. to absorb the organic Hg and through an acid $KMnO_4$ soln. to absorb metallic Hg. In both cases the Hg is determined photometrically at 605 mμ with dithizone. The method, which was developed for the analysis of vapours from the decomposition of organic mercurial fungicides in the soil, will determine 10 μg or more of alkyl mercury per 1000 litres of air in the presence of mercury vapour.
J. H. WATON

4839. **Determination of benzene and polymethylbenzenes.** S. H. Hastings and D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1960, **32** (4), 571.—Infra-red data are given for benzene and ten methyl derivatives.

4840. **Determination of C_8 alkylbenzenes.** D. E. Nicholson and S. H. Hastings (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1960, **32** (4), 571.—Infra-red data are given for ethylbenzene and the three diethylbenzenes.

4841. **Determination of C_{10} alkylbenzenes.** S. H. Hastings and D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1960, **32** (3), 441.—Infra-red data are given for 2-ethyl-1:4-dimethyl, 4-ethyl-1:3-dimethyl-, 4-ethyl-1:2-dimethyl- and 2-ethyl-1:3-dimethyl-benzene.

4842. **Chromatographic separation and ultraviolet analysis of polyphenyls.** W. W. West (California Research Corp., Richmond, Calif.). *U.S. Atomic Energy Comm.*, Rep. AECU-4699, Jan., 1960. 33 pp.—Relative adsorbabilities of polyphenyls and alkyldiphenyls in different solvent-adsorbent combinations were determined. A systematic study of the effects of solvent, adsorbent and structure type on adsorbabilities was made. Solvents with the greater eluting strengths were those having the higher dielectric constants. Both silica gel and alumina were found to be good for separating polyphenyls. Silica gel was the stronger adsorbent and was more useful for separating polyphenyls with two and three rings. By increasing the surface area of the silica gel, its adsorbing power was found to be increased. Sterically hindered polyphenyl isomers were adsorbed less strongly; those with increased resonance, *i.e.*, the *para* isomers, were adsorbed more strongly. Adsorbability data were used to develop a chromatographic procedure for the quant. separation of a known mixture of diphenyl, *o*-, and *m*-terphenyls and *m*-quaterphenyl. The two terphenyls were separated from each other only slightly, but the other separations were good. Product recoveries were 98% or greater. An accurate and rapid u.v. spectrophotometric method was devised to analyse soln. of polyphenyls. Polyphenyl absorption coeff. in *iso*octane were determined. Absorbances of individual polyphenyls were found to conform to the Bouguer-Beer law; absorbances of mixtures were additive. Wide ranges of concn. of polyphenyls, either singly or as mixtures, could be accurately calculated from absorbancy data.

NUCL. SCI. ABSTR.

4843. **Infra-red spectra of diphenyl and several deuterated diphenyls.** J. M. Scarborough (Atomics Intern. Div., N. American Aviation, Inc., Canoga Park, Calif.). *U.S. Atomic Energy Comm.*, Rep. NAA-SR-4657, March, 1960. 18 pp.—The infra-red solution spectra of diphenyl, diphenyl-2:2′:6:6′-$^3H_4$, diphenyl-3:3′:5:5′-$^3H_4$, diphenyl-2:2′:4:4′:6:6′-$^3H_6$, diphenyl-2:2′:3:3′:5:5′:6:6′-$^3H_8$, and diphenyl-$^3H_{10}$ are presented. All spectra were obtained on a spectrophotometer with LiF, NaCl and KBr optics.

NUCL. SCI. ABSTR.

4844. **Relative acidities of substituted phenols in pyridine and water.** C. A. Streuli (American Cyanamid Co., Stamford, Conn.). *Anal. Chem.*, 1960, **32** (3), 407–410.—Titration curves were plotted for 27 phenols and 17 other non-carboxylic organic acids in pyridine. Glass and methanolic calomel electrodes were used with an automatic titrimeter and the titrant was 0·1 *N* tetrabutylammonium hydroxide. All titrations were quant. except those of the aminophenols and biuret. The only polyhydric compound to show 2 equivalence points was phloroglucinol. Delta half-neutralisation potentials (Streuli and Miron, *Ibid.*, 1958, **30**, 1978) were calculated and are shown in a table together with the literature values for pK_a (H_2O). All the non-phenolic non-carboxylic compounds examined showed an increase in acidity in pyridine in comparison with carboxylic acids. Weakly acidic phenols gave steep titration curves. An equation relating the acidity of phenols in water and in pyridine is presented.

G. BURGER

4845. **Separation of halogenated phenols by paper chromatography.** H. S. Choguill and D. E. Bissing (Fort Hays Kansas State Coll., Hays, Kans., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 440.—The *o*- and *p*-isomers of chloro-, bromo- and iodo-phenols have been separated by two-dimensional chromatography with benzene-acetic acid-water (2:2:1) and HCl (20% w/v). Colours were developed by spraying with *p*-nitrophenyldiazonium fluoroborate, drying, and spraying with methanolic KOH soln. The colours and R_F values are tabulated.

G. BURGER

4846. **Photometric determination of 2:4:6-trichlorophenol.** R. U. Schenk (Cornell Univ., Ithaca, New York, U.S.A.). *Chemist Analyst*, 1960, **49** (1), 14–15.—Steam-distil the weighed sample (animal feeding-stuff or excreta) in the presence of Na_2CO_3 to remove interfering substances. Acidify with H_3PO_4 and steam-distil again. Pipette an aliquot of the distillate, containing $\geq$0·4 mg of 2:4:6-trichlorophenol, into a 100-ml flask. Add 25 ml of phosphate buffer (13·6 g of KH_2PO_4 in 1 litre at pH 7·6 to 8·0) and 1% 4-aminophenazone soln. (0·5 ml). Dilute to $\simeq$95 ml and shake, add 8% $K_3Fe(CN)_6$ soln. (0·25 ml) and dilute to the mark. Store away from light for 5 to 30 min., then measure the extinction at 500 to 525 mμ.

G. S. ROBERTS

4847. **Quantitative spectrophotometric determination of catechol, hydroquinone [quinol] and resorcinol in aqueous solutions.** J. Halmekoski (Inst. Chem., Helsinki). *Suomen Kem.*, 1959, **32** (12), 274–276 (in English).—A mixture of catechol (**I**), quinol (**II**) and resorcinol (**III**) is treated in suitable vol. with phosphate buffer (pH 7) (10 ml) and 0·1 *M* Na_2MoO_4 (5 ml) and H_2O to 100 ml. **I** is determined from the extinction at 412 mμ (Beer's law does not apply for amounts $<$0·08 mg per ml). **II** and **III** do not interfere. **I** can be pptd. with Pb acetate, removing excess of Pb as sulphate, and **II** and **III** can be determined in the filtrate. **II** can be determined with Folin-Denis reagent from the extinction at 800 mμ. **III** can be determined by treating an aliquot with Folin-Denis reagent (5 ml), 20% Na_2CO_3 soln. (20 ml) and H_2O to 50 ml. After heating the mixture at 30° for 30 min. the extinction is read at 720 mμ. The blue colour formed by **II** must be deducted. Alternatively, **III** can be determined by treating the soln. with $CHCl_3$ (10 ml) and 2 *N* NaOH (10 ml) and H_2O to 100 ml and heating at 57° for 1 hr., with occasional shaking. The extinction is read at 400 mμ; neither **I** nor **II** produces a colour.

R. M. S. HALL

4848. **Separation of [aromatic] acids [by paper chromatography].** L. V. Golosova and G. B. Ovakimyan. USSR Pat. 121,964 (18.8.59).—In separating benzenecarboxylic acids (*e.g.*, terephthalic and *iso*phthalic, *p*-toluic and terephthalic, or *m*-toluic and *iso*phthalic acids) by paper chromatography, the eluent used is water - propanol - 3% aq. NH_3 (105:350:12). The R_F values are—*iso*phthalic, 0·31 to 0·35; terephthalic 0·21 to 0·28; *m*-toluic 0·69 to 0·72; and *p*-toluic acid 0·76 to 0·81. The spots may be identified with bromothymol blue or optically. C. D. KOPKIN

4849. **Influence of magnesium ions on the ultraviolet absorption of aqueous solutions of salicylic acid and related compounds.** C. A. Zittle, L. Pepper and E. W. Bingham (Eastern Regional Res. Lab., Philadelphia, Pa., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **88** (1), 94–97.—Addition of Mg^{2+} to aq. solutions of salicylic acid and of methyl salicylate is found to shift the max. to longer wavelengths and to cause an increase in extinction. The effect is marked only at high pH values, the influences of which are also considered.
W. H. C. SHAW

4850. **Polarographic behaviour of aryl sulphones and sulphoxides.** R. C. Bowers and H. D. Russell (Northwestern Univ., Evanston, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 405–407.—The reduction of methyl phenyl sulphone, phenyl sulphone, methyl phenyl sulphoxide and phenyl sulphoxide at the dropping mercury electrode with 0·1 *M* tetramethylammonium bromide in 50% aq. ethanol as supporting electrolyte has been studied. The reaction was also followed coulometrically and the number of electrons involved was found to be 2. The u.v. spectra of the products were examined. The results confirm that the products from the aryl sulphones are the corresponding arylsulphinic acids and those from the aryl sulphoxides are the aryl sulphides. G. BURGER

4851. **The detection and differentiation of phenyl hydrogen sulphate and phenolsulphonic acid by spot analysis.** F. Feigl and V. Anger (Min. Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1960, (3), 409–411 (in German).—Phenol is liberated when phenyl hydrogen sulphate is heated with dil. mineral acids, and phenol and 1-naphthol, respectively, are liberated when phenolsulphonic acids and 1-naphtholsulphonic acids are heated to 220° with succinic or phthalic acid. The phenol vapours are detected by the indophenol reaction with 2:6-dichloro-*p*-benzoquinone-4-chlorimine.
T. R. ANDREW

4852. **The vibrational spectra of phenyl thiocyanate and benzoyl *iso*thiocyanate.** N. S. Ham and J. B. Willis (Div. of Chem. Phys., C.S.I.R.O., Chem. Res. Lab., Melbourne, Australia). *Spectrochim. Acta*, 1960, **16** (3), 393–395.—The Raman and i.r. spectra of these compounds confirm the identification of the previously reported characteristic *iso*thiocyanate bands (*Ibid.*, 1960, **16**, 279).
P. T. BEALE

4853. **The titration of aromatic boron compounds with mercuric ions.** A. Heyrovský (Charles' Univ., Prague). *Z. anal. Chem.*, 1960, **173** (4), 301–309 (in German).—The titrations are carried out in 0·1 *N* Na acetate, with $Hg(NO_3)_2$ or $Hg(ClO_4)_2$ soln. as titrant, and the end-points are detected potentiometrically with a mercury-coated platinum electrode and the S.C.E. joined by an agar bridge, or amperometrically with a dropping mercury electrode *vs.* the S.C.E. Examples are given of the titration of Na tetraphenylboron, triphenylboron, diphenyl hydrogen borate and phenyl dihydrogen borate. Compounds containing more than one phenyl group react in two stages, indicated by two separate increases in potential. The reverse titration of Hg^{2+} with Na tetraphenylboron is also possible.
W. T. CARTER

4854. **Determination of microgram quantities of some phenylmercury compounds and their separation from inorganic mercury salts.** E. Hoffmann (C.S.I.R.O., Div. of Building Res., Highett, S.21, Victoria, Australia). *Z. anal. Chem.*, 1960, **174** (1), 48–50 (in English).—Phenylmercury compounds react with diphenylcarbazone in the same way as do inorganic mercury compounds, but are resistant to reduction by zinc dust. To the sample soln. (1 ml) add water (2 ml) and 1% ethanolic diphenylcarbazone soln. (1 drop). After 2 min. add phosphate buffer (pH 6) (2 ml) and measure the colour against standards (up to 13 μg of Hg). This gives total Hg. Repeat after shaking the sample soln. with zinc powder for 40 min. and record the Hg as "phenylmercury." Inorganic Hg is determined by difference. T. R. ANDREW

4855. **Volumetric determination of 1-naphthol with sodium nitrite.** M. Matrka (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 964–965 (in Russian).—*Procedure*—Dissolve the sample (1·44 g) in *N* NaOH (50 ml) and dilute with H_2O to 100 ml. To 10 ml add a soln. of Na *m*-xylenesulphonate (20%) (50 ml) and HCl (15 ml), and titrate potentiometrically with 0·1 *N* $NaNO_2$. J. ZÝKA

4856. **Colorimetric determination of traces of acids in dimethyl terephthalate.** A. L. Hensley [Res. and Dev. Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1960, **32** (4), 542–543.—The sample, containing an amount of acid equivalent to 0·05 to 0·20 mg of KOH, is dissolved in about 75 ml of solvent mixture (toluene - dimethylformamide) (1:3), and 2 ml of bromophenol blue (**I**) indicator soln. (0·4 g of **I** in 500 ml of dimethylformamide containing sufficient 0·5 *N* ethanolic KOH to give a dark blue soln.) is added. The mixture is made up to 100 ml and the extinction is measured within 1 hr. The acid equivalent in mg of KOH is read from a previously prepared calibration curve. The method is accurate, rapid and sensitive, with an acid value detection limit of 0·003 mg of KOH per g. Since the indicator soln. fades slowly the calibration curve should be checked daily and the solvent mixture should be prevented from absorbing CO_2 from the atmosphere. By choice of suitable solvents and indicators the scope of the procedure could be extended to the determination of the acid value of other non-acid substances, such as edible oils, turbine oils, and most organic solvents.
S. M. MARSH

4857. **Electromigration methods. II. Relation between the structure of anthraquinone derivatives and their mobility in paper electrophoresis.** J. Franc and M. Wurst (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 657–661 (in German).—The influence of steric configuration of anthraquinone derivatives on the direction of mobility in paper electrophoresis was studied. For the detection of

the derivatives, this method was combined with paper chromatography, which was carried out on Whatman No. 1 paper impregnated with a 30% petroleum (boiling-range 190° to 275°) soln. in light petroleum, with the use of the descending technique; 80% ethanol was used as the mobile phase. The R_F values of numerous anthraquinone derivatives were determined. The separated spots were observed in u.v. light. Paper electrophoresis was carried out in 3 *N* aq. NH_3 and *N* acetic acid as electrolyte with a potential drop of 6 to 7 V per cm.
J. ŽÝKA

4858. **Application of optical polarimetry and density measurements to the analysis of a ternary mixture.** J. E. Hawkins and J. W. Vogh (Dept. of Chem., Univ. of Florida, Gainesville, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 437–438.—A relatively rapid method is described for determining the composition of a ternary mixture produced during the thermal isomerisation of β-pinene. Only measurements of density and optical rotation are necessary. The method might be extended to systems containing more components by the measurement of other physical constants.
K. A. PROCTOR

4859. **Analysis of isomeric menthols by gas chromatography.** Waichiro Tagaki and Tetsuo Mitsui (Dept. of Agric. Chem., Kyoto Univ., Japan). *Bull. Agric. Chem. Soc. Japan*, 1960, **24** (2), 217–218 (in English).—The partial separation of a mixture of four isomeric menthols is achieved by the use of a polyoxyethylene glycol column (0·6 cm × 3 metres) at 160°, with He as carrier gas and a flow rate of 59 ml per min. Separate peaks are obtained for (+)-neomenthol and (+)-*iso*menthol, but a mixture of (−)-neo*iso*menthol and (−)-menthol is not further resolved, and gives a single peak.
H. B. HEATH

4860. **Determination of traces of propyne and propadiene in cracked gases by gas chromatography.** G. Heuschkel, J. Wolny and S. Skoczowski (Esso Raffinerie, Hamburg). *Erdöl u. Kohle*, 1960, **13** (2), 98–99.—The gas to be analysed was a mixture of propane and propylene containing up to 0·5% of C_4 hydrocarbons with traces of propyne and propadiene. A first separation was made on a column of silicone oil (25%) on Sterchamol. The fraction containing the propyne and propadiene was collected in a cold trap (liquid N) and completely separated on a column of diethylformamide (20%) on Sterchamol.
G. BURGER

4861. **Determination of sulphur dioxide and hydrogen sulphide in generator gas.** S. A. Kiss (Chem. Co. of Borsod, Hungary). *Magyar Kém. Lapja*, 1960, **15** (3), 136–137.—Sulphur dioxide is oxidised to H_2SO_4 with H_2O_2 soln. and subsequently titrated acidimetrically. The unchanged H_2S is converted into CdS and determined iodimetrically. The accuracy is within 0·5%.
G. SZABO

4862. **Gas-chromatographic determination of *n*-pentane and lighter components in olefin-free naphthas using ethyl chloride as an internal standard.** H. D. LeRosen (Texaco, Inc., Port Arthur, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 444–445.—The light components of naphtha were determined within 10% on a chromatograph modified to allow reversal of the carrier-gas flow. Perkin-Elmer columns C (silicone 200 on Celite) and D (tetra*iso*-butylene on Celite) were combined in that order. Ethyl chloride, measured by vol., was added as internal standard; the carrier gas used was He at 83 or 150 ml per min. at room temp. The gas flow was reversed for 20 min. after the elution of *n*-pentane. The time required for analysis is 1 hr.
G. BURGER

4863. **Gas-chromatographic analysis of olefinic naphthas in the three- to six-carbon range with the aid of a subtraction technique.** R. L. Martin [Standard Oil Co. (Indiana), Whiting, Ind., U.S.A.]. *Anal. Chem.*, 1960, **32** (3), 336–338.—In the gas chromatography of naphthas containing olefins some of the olefin peaks overlap those of saturated hydrocarbons. To avoid this interference two successive runs are made. In the first a short column filled with silica gel coated with H_2SO_4 is inserted between the column and the detector. Olefins are thus absorbed and the peaks for the saturated components are registered. The second run is made without the absorber and the olefin and saturated hydrocarbon peaks are registered together. The olefins are then determined by difference. Alternatively, two chromatograms can be made in one run, with the absorber fitted between two matched detectors.
G. BURGER

4864. **Determination of sulphur in organic products by combustion in a high-frequency furnace.** A. Le Berre and J. Léger (Lab. de Chim. Org. des Hormones, Collège de France). *Chim. Anal.*, 1960, **42** (4), 191–194.—The A.S.T.M. method for the determination of S in petroleum products is modified by covering the conductor (iron powder) with quartz wool to avoid loss, instead of using tin and the crucible lid. In a further modification the iron conductor (which must be extremely pure) is replaced by a tablet of carborundum which rests across or in the top of the crucible. This substitution permits a simpler, easier and more rapid procedure; the layer of MgO over the sample may be omitted and both the crucible and the conductor may be used again many times. The SO_2 evolved is absorbed in an acidified soln. of KI and starch, and is titrated with KIO_3. A correction factor of 1·07 (iron method) or 1·10 (carborundum method) must be applied.
J. H. WATON

4865. **Determination of sulphur in petroleum products by hydrogenation.** E. C. Schluter, jun., E. P. Parry and G. Matsuyama (Union Oil Co. of California, Union Res. Center, Brea, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 413–417.—Apparatus and procedure are described for the determination of S, in the concn. normally found in petroleum, with an accuracy equal to that of the lamp method. Halogens, N, P and As in concn. normally encountered do not interfere. The sample is heated in a stream of moist H and the gases are passed over a nickel catalyst at 1200°. The H_2S produced is absorbed in 0·1 *N* NaOH and determined by amperometric titration with 0·2 *N* $HgCl_2$ or, if the concn. is <0·1%, by the methylene blue method. As little as 1 p.p.m. of S can be determined. The method can also be used for the determination of inorganic S and of halogens in petroleum. A determination requires 30 to 45 min.
G. BURGER

4866. **Rapid determination of phosphorus in gasoline. Spectrographic and colorimetric methods.** M. E. Griffing, C. T. Leacock, W. R. O'Neill, A. L. Rozek and G. W. Smith (Ethyl Corp., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 374–379.

—Each of the methods described is applicable in the presence of other additives used in petrol. The spectrographic method is suitable for concn. between 5 and 75 mg per litre. The instrument used was a modified grating spectrometer fitted with a rotating carbon electrode and a means of passing Ar across the boat containing the sample. The sample (4 ml) is mixed with an internal standard - radiation buffer (6 ml) prepared by dissolving triphenylarsine (1·43 ml) in a mixture of *iso*propyl alcohol (400 ml) and dimethylformamide (600 ml). The intensity of the P line at 2535·65 A is compared with that of the As line at 2456·53 A. If Mn is present a correction must be made, which is obtained from the line at 2551·88 A. Two operators can make 70 determinations per day with a standard deviation of 0·8 mg per litre. In the colorimetric procedure the sample (1 g) is mixed with ZnO (2 g) and ignited. The P is determined in the presence of the Zn by the molybdenum blue method. A single determination requires 1 hr. One operator can make 24 determinations per day with a standard deviation of 0·5 mg per litre. This method is applicable to concn. between 5 and 50 mg of P per litre.

G. BURGER

4867. **Countercurrent distribution of high-boiling phenols from a low-temperature coal tar.** C. Karr, jun., P. A. Estep and L. L. Hirst, jun. (Low-Temperature Tar Lab., Bureau of Mines, U.S. Dept. of the Interior, Morgantown, W. Va.). *Anal. Chem.*, 1960, **32** (4), 463–475.—Tar acids, boiling-range 231° to 331°, were separated into ten preliminary fractions by distillation, and each fraction was further separated by countercurrent distribution. An automatic apparatus was used and the solvents were *cyclo*hexane and a phosphate buffer of pH varying between 9·94 and 11·86 according to the type of phenol suspected in the fraction. Constituents were identified by infra-red and ultra-violet spectra and comparison of partition coefficients with those of known phenols. Of the 84 compounds shown to be present, 24 were specifically identified and 36 were assigned a structural type. Results are detailed in graphs and tables. The methods used for the identification of alkylphenols, alkenylphenols, *cyclo*alkylphenols, indanones, indanols, indenols, naphthols and fluorenols are described in considerable detail.

S. M. MARSH

4868. **Polarographic determination of thiosulphate in photographic gelatin.** V. Štefan (Spolana, Neratovice, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (3), 126–129.—*Procedure*—To 5 g of the sample add 0·1 *M* KNO_3 (95 ml); after 1 hr. dissolve by immersion of the flask in a water bath at 50°. Transfer an aliquot (20 ml) to the polarographic vessel, remove O with a stream of N and register the anodic - cathodic wave at 30° from −0·5 V. Evaluate the results by means of the method of standard addition. The method yields good results for concn. of $S_2O_3^{2-}$ from 6×10^{-4} to 3×10^{-3} *M*, with a mean error of ±5%. Iodides and tetrathionates interfere.

J. ZÝKA

4869. **Colorimetric determination of ionic detergents.** E. S. Abramovich. USSR Pat. 122,336 (25.8.59).—Methyl violet or Brilliant green decolorised with Na_2SO_3 is used as indicator; in 0·005% aq. soln. they become blue - violet or bright yellow in the presence of ionic detergents. Electrolytes or water-softening agents do not interfere. With C_{11-13} ionic detergents the sensitivity is 0·1 to 0·2 mg with methyl violet and 0·3 to 0·4 mg with Brilliant green; the accuracy (with a photo-electric colorimeter) is within ±3%. *Procedure*—Place 1 ml of the aq. detergent soln. and 4 ml of reagent soln. (1 vol. of dyestuff and 2 vol. of 5% aq. $Na_2SO_4.7H_2O$) in a test-tube with a ground glass stopper, shake, set aside for 20 min., and compare the colour (using a blank) with a standard calibration curve.

C. D. KOPKIN

4870. **Colorimetric determination of anionic detergents.** L. Benšek and A. Galle (Res. Inst. of Wool, Brno, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (3), 139–141.—The method is based on the formation of a coloured complex from the detergent and methylene blue, and its extraction.

J. ZÝKA

4871. **Analysis of surfactant mixtures.** L. E. Weeks and J. T. Lewis (Monsanto Chemical Co., St. Louis, Missouri). *J. Amer. Oil Chem. Soc.*, 1960, **37** (3), 138–142.—Methods are described by which surfactants can be isolated from detergent compositions and separated and characterised as non-ionic, sulphonates, sulphates and hydrotropes. Results were found to be in good agreement with expected values.

I. DICKINSON

4872. **Method for determining non-ionic surface-active agents in oils and solvent extracts from wool.** B. C. Hobson and R. S. Hartley (Wool Industries Res. Ass., Torridon, Headingley, Leeds, England). *Analyst*, 1960, **85**, 193–196.—The sample of oil or solvent extract from wool (≡10 to 100 mg of the non-ionic compound) is shaken with 5 ml of ethanol and 5 ml of $BaCl_2$ soln. (10%) and the mixture is applied to an alumina column which is eluted with water, the eluate being filtered as it is collected. The eluate is treated with 5 ml each of dil. HCl, $BaCl_2$ soln. and molybdophosphoric acid soln. in that order, boiled and then set aside overnight. The ppt. is collected in a sintered porcelain crucible, washed with water, ethanol and ether, dried at 100° and weighed. The amount of non-ionic compound present is calculated from a calibration graph prepared from the compound if its identity is known, or from a specific product, *e.g.*, Lissapol NX or Ethylan CP. Recovery of known amounts was satisfactory.

A. O. JONES

4873. **Fiore method for determining linalol: amendment.** Analytical Methods Committee of The Society for Analytical Chemistry. Essential Oils Sub-committee. *Analyst*, 1960, **85**, 165.—In a previous report (*Ibid.*, 1957, **82**, 325) the respective merits of the Fiore and Glichitch methods were discussed, and, on the evidence then available, the latter method was recommended. Development of gas - liquid chromatography has provided improved means of studying the reactions in both methods (Holness, *Ibid.*, 1959, **84**, 3), and it is found that results by the Glichitch method are consistently biased, being ≃4% lower than the true value, whereas results by the Fiore method are biased in the same direction by only ≃1%. The Fiore method is therefore now the recommended method.

A. O. JONES

4874. **Quantitative determination of free menthol in peppermint oil.** M. I. Blake (School of Pharmacy, N. Dakota Agric. Coll., Fargo). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (3), 175–177.—Esterify the menthol in the sample (400 to 500 mg) by heating with chloroacetyl chloride (1 g) at 101° or 102° in toluene soln. Stir magnetically and pass a constant

stream of N so as to sweep the liberated HCl into a trap containing 0·05 *N* $AgNO_3$ (50 ml) and determine by the Volhard method. The results are comparable with those obtained by the U.S.P. method and by the method of Hamarneh *et al.* (*Anal. Abstr.*, 1957, **4**, 1653). Two determinations and a blank require between 4 and 5 hr.

A. R. ROGERS

4875. **Coulometric micro-determination of thymol in the substance, also in *Thymus vulgaris* L. and its oil.** Z. Kalinowska (Dept. Pharm. Chem., Med. Acad., Łódź, Poland). *Acta Polon. Pharm.*, 1960, **17** (2), 153–158.—By using electrolytically generated bromine, thymol can be determined coulometrically in amounts >0·5 mg with an accuracy of ±0·5% on a 0·5-g sample of the dried herb. Thymol is determined coulometrically in the herb after steam-distillation in a specially designed apparatus, and the electrolysis cell is modified in such a manner that the escape of Br from the vessel is prevented by the use of a cathode arm in which the liquid acts as a catholyte and as a safety valve against oxidation of Br. It was established that after a year's storage of the oil under normal conditions, the content of volatile phenols increased by 10%, and that the dry herb stored in paper bags for the same period showed up to a 20% loss of volatile phenols.

W. B. MIASKOWSKI

4876. **Urea adducts from civet and other volatile or concrete oils. A new analytical and preparative method.** F. Wolf (Anal. Dept., VEB Chem. Fabrik Miltitz, Leipzig). *Riechstoffe u. Aromen*, 1960, **10** (3), 69–71.—To determine the contents of pure oil and of waxy constituents and waxy adulterants in volatile or concrete oils, the sample is treated with a soln. of urea in methanol - benzene (3:2) (**I**) to form an insol. adduct of urea with the waxy compounds; the adduct is filtered off and decomposed to liberate the waxy compounds; the oil is recovered from the filtrate. *Procedure*—For civet, the sample (10 g) is treated at 0° with 60 g of urea dissolved in 80 ml of **I**; after 3 to 5 hr. the adduct is filtered off and decomposed to liberate the waxy compounds, and the oil is recovered from the filtrate by adding water to throw the oil out of solution, and then separating the oil layer. For oils of cassia, lavender, rose, iris, jasmine and geranium the procedure is similar, but when the oil contains compounds sol. in the diluted **I** the recovery of the oil from the filtrate is effected by distilling off most of the solvent, adding a little water to the residue, and then extracting the oil with ethyl ether.

H. L. WHITEHEAD

4877. **Interference of ketones in the estimation of perfumery alcohols in synthetic mixtures by acetylation. I.** J. B. Lal, A. P. Mathur and V. M. Patwardhan (Chem. Engng Sect., H.B. Technol. Inst., Kanpur). *J. Oil Technol. Ass. India*, 1958 [1959], **14** (2), 9–20.—The determination of benzyl alcohol, phenylethyl alcohol, geraniol and santalol in the presence of 20 to 80% of acetophenone by acetylation with acetic anhydride - sodium acetate has been studied at reaction temp. from 80° to 140°. The results varied from being 3 to 6% high in the case of benzyl alcohol to ≃35% high for santalol. A side reaction of acetophenone with the alcohol accounts for this interference, which depends on the number of alcoholic active methylene groups present. Detailed analytical data for different binary mixtures are tabulated.

P. M. KINGSTON

4878. **The analysis of [cosmetic] creams.** I. Hajdu (State Factory for Perfumes and Soaps, Budapest). *Parfums, Cosmét. Savons*, 1960, **3** (3), 103–107 (in French).—Methods are described for the determination of water and total fatty matter and, in stearate creams, total neutral fatty matter, total and combined stearic acid (by gravimetric and volumetric methods) and glycerol.

N. E.

4879. **Paper chromatography of water-soluble synthetic dyes.** K. Woidich, T. Langer and L. Schmid (II Chem. Univ.-inst., Wien). *Dtsch. Lebensmitt-Rdsch.*, 1960, **56** (3), 73–79.—A literature survey is presented, dealing with column and paper chromatography. R_F values are tabulated for 70 dyestuffs with 5 different solvent mixtures. (50 references.)

I. DICKINSON

4880. **Paper chromatography of water-soluble dyes.** J. C. Riemersma and F. J. M. Heslinga (Lab. Med. Chem., Univ. Leiden, Netherlands). *Mitt. Lebensmitt. Hyg., Bern*, 1960, **51** (1), 94–104.—In cases where two food dyes are present that are difficult to separate chromatographically, it has proved valuable to carry out two different techniques from which different R_F values are obtained. In addition to the method developed by Thaler and Sommer (*Z. Lebensmitt Untersuch.*, 1953, **97**, 345) the solvent *tert.*-butyl alcohol - propionic acid - water (25:6:19) containing 0·4% of KCl has been used by an ascending technique. It was found unnecessary to establish an equilibrium. Dye soln. (0·1% either in H_2O or in 50% ethanol) (3 µl) was applied on the starting line 3 cm from the bottom end of the paper and dried for 30 min. The temp. was kept at 19° to 20° and the running time was 7 hr. Forty-nine dyes were chromatographed and their R_F values determined. The reproducibility was good and the spots were sharply defined.

I. DICKINSON

4881. **Polarographic study of hydroxytriphenylmethane dyes.** M. Matrka, F. Navrátil and C. Fišar (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (3), 129–132.—The polarographic behaviour of aurine, Eriochrome azurol BC (C.I. Mordant Blue 1), Chromoxane blue R (C.I. Mordant Blue 42), Chromoxane brown 5R (C.I. Mordant Brown 26) and Naphthochrome azurine B (C.I. Mordant Blue 28) was studied, the dependence of the two-step reduction on pH examined and the corresponding $E_{\frac{1}{2}}$ values determined. The results obtained were used for the analytical evaluation of the dyes studied. *Procedure*—To 1 ml of an ethanolic soln. of the sample (≃0·0005 *M*) add gelatin soln. (0·5%) (0·5 ml), ethanol (2 ml) and buffer soln. of pH 7, de-aerate with N, register the polarographic wave and compare with a calibration curve.

J. ZÝKA

4882. **Methods for the determination of starch in bandages.** A. Simkova and A. Haller (Staatsanst. für Arzneimittelkontrolle, Prague). *Pharm. Zentralh.*, 1960, **99** (3), 113–115.—The method recommended involves hydrolysis of the starch and titration of the glucose produced. *Procedure*—Heat the sample (0·7 or 0·8 g) under reflux with 25% HCl soln. (16 ml) and H_2O (150 ml) for 90 min., neutralise to methyl orange with 50% KOH soln. and dilute to 250 ml with H_2O. To a 25-ml aliquot add Fehling's soln. (20 ml), heat rapidly to boiling, boil for 2 min., cool rapidly, add KI (3 g) and 25% H_2SO_4 soln. (25 ml) and titrate with 0·1 *N* $Na_2S_2O_3$, with starch as indicator. Perform a blank titration.

A. R. ROGERS

4883. **New rosin and lignin reactions for the identification of fibrous raw materials in paper.** E. Kühnel. *Papier, Darmstadt*, 1960, **14** (3), 96–99.—Certain blue dyes of the triphenylmethane group give staining reactions with lignin-containing fibres but do not affect lignin-free fibres. This differential reaction is useful, *e.g.*, in testing viscose-grade pulps, in which the presence of lignin can lead to filtration difficulties. By using soln. containing a blue dye in combination with other dyes, such as a substantive (direct) dye for cellulose, all the fibres of a preparation can be stained in one step. Those fibres containing lignin can then be differentiated from those free from lignin by examination under the microscope. A simple new test for rosin, based on treatment with iodine vapour, is described, in which the depth of the brown colour developed is correlated with the rosin content of a sample. This test can show the distribution of both natural rosin and rosin size within the fibres and is also applicable to finished papers. It is especially suitable for differentiating bleached sulphite (rosin-containing) from bleached kraft (rosin-free) softwood pulps.

ABSTR. BULL. INST. PAPER CHEM.

4884. **Estimation of basic groups in wool by dye-uptake measurements.** J. A. Maclaren [Wool Res. Lab. C.S.I.R.O., Parkville N.2 (Melbourne), Victoria, Australia]. *Arch. Biochem. Biophys.*, 1960, **86** (2), 175–178.—In the method described, the wool sample (25 mg) is treated in a stoppered test-tube with 10·0 ml of a soln. (7 milli-equiv. per litre) of purified Orange II (C.I. Acid Orange 7) in anhydrous formic acid for 1 hr., with occasional shaking. A 1·0-ml aliquot is then diluted to 500 ml with water and the difference in extinction (E diff.) measured at 485 mμ is compared with the extinction of the original dye soln. similarly diluted. Then, dye uptake (milli-equiv. per g) = (E diff.) × 43·60 × 10/2W, where W is the dry weight of sample taken. The dye is purified by triple recrystallisation of the commercial product from water and by passage as a 1% soln. through a column of Zeo-Karb 225 resin (H^+ form). The eluate is evaporated to dryness *in vacuo* on a steam bath and then dried *in vacuo* over P_2O_5. The method is applicable to chemically modified wool.

W. H. C. SHAW

4885. **Polarographic determination of the elementary and sulphide sulphur in viscose fibres.** R. Pečený and V. Nedvědová (Severočeské Chemické Závody, Lovosice, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (3), 165–167.—The method is based on the conversion of the total S into sulphide S in NaOH soln. at 95° to 100° and polarographic determination of the sulphide S in the alkaline extract of the fibre. The combined S can be removed from the fibre by decomposition with H_2SO_4 and the elementary S is subsequently determined; the relative error is ±5%. *Procedure for total S*—Place the sample of the fibre into a mixture of N NaOH (9 ml) and H_2SO_4 (10%) (1 ml); add $Na_2S_2O_3$ soln. (10%) (0·5 ml) and a soln. of EDTA (5% in 0·1 N NaOH). Remove O with a stream of N, close the tube with a valve tube containing 0·5 ml of the EDTA soln. and heat for 30 min. on a water bath. Cool to 20°, stir with a stream of N, transfer to the polarographic vessel and register the wave from −0·2 V to −1·0 V. *Procedure for elementary S*—Heat the sample with H_2SO_4 (10%) (1 ml) for 30 min. at 70° on a water bath. Remove H_2S and CS_2 with a stream of N, cool, add N NaOH (9 ml), close the tube with a valve tube and proceed as described above. The following weights of sample were used—0·5 g for 0·005 to 0·05% of S; 0·10 g for 0·05 to 0·30%, and 0·05 g for 0·30 to 0·60%.

J. ZÝKA

4886. **Analysis of methyl methacrylate copolymers by gas chromatography.** J. Strassburger, G. M. Brauer, M. Tryon and A. F. Forziati (Dental Res. Sect., Nat. Bur. of Stand., Washington, D.C., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 454–457.—Chromatographic analysis of the liquid pyrolysis products obtained by depolymerisation in air can be used for the detection of small amounts (0·2%) of copolymeric constituents, and aids in the identification and characterisation of the components of copolymers and polymer mixtures. The sample is pyrolysed on hot coils surrounded by the carrier gas, and components can be determined with a precision of ±5% from standard curves of the ratio of peak areas at known composition. The chromatography is carried out on a 6-ft. column of 25% of dinonyl phthalate on 30 to 70-mesh firebrick with a helium flow of 50 ml per min. at 140°.

K. A. PROCTOR

4887. **Polarographic determination of styrene monomer in polyester resins.** W. M. Ayres and G. C. Whitnack (U.S. Naval Ordnance Test Sta., China Lake, Calif.). *Anal. Chem.*, 1960, **32** (3), 358–360.—Styrene can be determined at the dropping mercury electrode with a supporting electrolyte of tetrabutylammonium chloride in ethanol. A sample (250 to 500 mg) of the polyester resin is shaken with 50 ml of 95% ethanol and the soln. is made up to 100 ml with 95% ethanol. An aliquot (5 ml) is added to a mixture of 10 ml of 95% ethanol and 5 ml of 0·1 M aq. tetrabutylammonium chloride, and a polarogram is recorded from −2 V to −2·8 V. The $E_{\frac{1}{2}}$ of styrene is −2·53 V *vs.* the S.C.E. No interference is caused by O or by phthalate, fumarate or maleate esters. The confidence limits (95% level) are ±0·5% of styrene.

G. BURGER

4888. **Determination of traces of hydroperoxide by reaction with arsenic(III). Application to determination in polymer latex.** I. M. Kolthoff, E. J Meehan, S. Bruckenstein and H. Minato (Univ. Minnesota, Minneapolis, U.S.A.). *Microchem. J.*, 1960, **4** (1), 33–41.—Two methods are described, both of which depend upon reaction in alkaline medium. In one, a slight excess of As^{III} is used, the soln. is heated to boiling, then cooled, and the excess of As^{III} is determined by amperometric titration with iodine. In the other, a large excess of As^{III} is added and the reaction is carried out at room temp. in the absence of air. The amount of As^{V} is determined spectrophotometrically by the molybdenum blue procedure. The latter method is applied to the analysis of polystyrene latex after extraction of the hydroperoxides into benzene - light petroleum (2:1). Errors are $\gtrsim \pm 2{\cdot}5\%$ for the spectrophotometric and $\gtrsim \pm 0{\cdot}5\%$ for the amperometric method at the 10^{-5} M level.

G. P. COOK

4889. **The infra-red spectra and molecular configurations of polyamides.** C. G. Cannon (Res. Dept., British Nylon Spinners Ltd., Pontypool, Mon.). *Spectrochim. Acta*, 1960, **16** (3), 302–319.—The i.r. spectra of a wide variety of polyamides of diamine - diacid and ω-amino acid type are reviewed. The amide - amide dipole interaction is the dominant factor controlling the packing and configurations of the molecules. Complete association occurs in all polymers and copolymers. This

imposes a distortion on the hydrocarbon segments out of the planar zig-zag configuration in the copolymers with differing repeat unit lengths, and in the diamine - diacid polymers with odd numbers of CH_2 groups in either or both sections of the repeat unit. Attempts to explain melting-point variations in polyamides on the basis of assumed planar chain configurations and differing extents of CONH association are not supported by the spectroscopic evidence. P. T. BEALE

4890. **Chromatography of organic compounds. V. Determination of phenylchlorosilanes by gas chromatography.** J. Franc and M. Wurst (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 701–705 (in German).—Technical mixtures of benzene, chlorobenzene, phenyltrichlorosilane, diphenyl and diphenyldichlorosilane encountered in the manufacture of silicones are chromatographically separated at 240° on a column of Chromosorb impregnated with 20% of Silicone-elastomer E 301 (Griffin and George). The issuing gases are burnt to CO_2 and H_2O in a combustion tube, the CO_2 is absorbed, and the H_2O is reduced to H with heated iron turnings and detected by thermal conductivity. J. ZÝKA

4891. **Determination of silicon in polyaluminoorganosiloxane resins.** Ya. I. Chulkov. USSR Pat. 121,963 (18.8.59).—The resin is decomposed with fuming H_2SO_4 in the presence of $(NH_4)_2SO_4$, the soln. is diluted, and Al is complexed with tartaric acid. *Procedure*—Heat 0·2 g of dry finely ground resin and 0·2 g of $(NH_4)_2SO_4$ in a quartz crucible while adding fuming H_2SO_4 dropwise. Silicic acid is pptd. Cool, transfer the mixture to a beaker containing 25 ml of 2% tartaric acid soln., add a few drops of methyl red soln., heat to boiling, and add aq. HN_3 (1:1) till alkaline. Stir, boil for 2 min., allow to cool, decant the liquor, and wash the residue twice by decantation with hot water (test the washings for dissolved solids by evaporation). Transfer the ppt. back to the quartz crucible, ash the filter-paper, dehydrate the silicic acid at 800°, ignite to constant wt. at 1000° to 1050°, and weigh the SiO_2. C. D. KOPKIN

4892. **Infra-red spectroscopy of surface coatings in reflected light.** H. Dannenberg, J. W. Forbes and A. C. Jones (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 365–370.—Organic surface coatings deposited on metal surfaces can be qual. and semi-quant. analysed by an i.r. procedure in which the i.r. beam passes through the coating, is reflected from the substrate, passes through the coating again, and then enters the spectrophotometer. This method, for which a commercial instrument, equipped with a special reflectance accessory (illustrated), is used, produces good spectra of clear surface coatings, 0·1 to 0·5 mil thick, on flat surfaces of specularly reflective metals such as tin-plated steel, cold-rolled steel, aluminium and brass. K. A. PROCTOR

4893. **Colorimetric identification and estimation of phenolic antioxidants.** C. L. Hilton (Res. Center, U.S. Rubber Co., Wayne, N.J.). *Anal. Chem.*, 1960, **32** (3), 383–387.—The sample of natural or synthetic raw or cured polymer is extracted for 16 hr. with 95% ethanol or methanol. The extract is coupled with diazotised *p*-nitroaniline and the absorption spectrum is determined from 700 mμ to 400 mμ. The compound is identified by the wavelength of the absorption max. and the amount is determined from the extinction. The trade name, composition, absorptivity and wavelength of the absorption max. in the visible region are tabulated for 26 antioxidants and their spectra are shown graphically. Other compounding ingredients do not interfere. Mixtures of phenolic antioxidants cannot usually be identified, but the amounts can be determined if the identities are known. The method is not applicable to highly oxidised samples. G. BURGER

4894. **Analysis of explosives using infra-red spectroscopy.** F. Pristera, M. Halik, A. Castelli and W. Fredericks (Propellants and Explosive Lab. of Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 495–508.—The physical constants and infra-red spectra of 68 common high explosive compounds, additives and related compounds are presented. Methods for the qualitative analysis of single ingredients and of mixtures, and for the quantitative analysis of mixtures are outlined. Useful spectral correlations and solubility data are included. (27 references.) S. M. MARSH

See also Abstracts—**4652**, Determination of glucose. **4686**, Mercury in org. compounds. **4688**, Boron in organoboron compounds. **4835**, Detection of esters of non-carboxylic acids. **4931**, Separation of long-chain aldehydes. **5035**, Separation of fatty acids. **5040**, Detection of phosgene. **5052**, Separation of chloromethylphenoxyacetic acids. **5053**, Analysis of esters of trichlorophenoxy-acetic acid. **5068**, Schöniger flask. **5117**, Elementary analysis. **5119**, S in petroleum.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

4895. **New clinical method for measuring dissolved and bound oxygen in blood electrochemically.** K. Damaschke and E. Saling (Bundesanstalt f. Materialprüfung, Berlin-Dahlem). *Klin. Wochschr.*, 1959, **37** (15), 826–828.—A special apparatus is described. The measuring electrode (cathode) is gold amalgam, and the reference electrode (anode) is zinc. The anode is contained in a tube containing saturated KCl soln. and is connected through a diaphragm with the measuring soln. (phosphate buffer) which contains the cathode. The current generated by reduction of the oxygen in the sample to OH^- is directly proportional to the oxygen content and is measured with a sensitive galvanometer. H. F. W. KIRKPATRICK

4896. **Easy method for the determination of the pCO_2 of the blood.** D. Mendel (Inst. of Cardiology, London, England). *Lancet*, 1960, **i**, 807.—A portable syringe-electrode system for blood pH determination, previously described (*Ibid.*, 1957, (i), 1125), is modified for pCO_2 measurement. The technique is described in detail. H. F. W. KIRKPATRICK

4897. **Volumetric method for serum sodium.** P. Oesper and C. J. Pauerstein (Dept. of Biol. Chem., Hahnemann Med. Coll., Philadelphia, Pa., U.S.A.).

Clin. Chem., 1959, **5** (6), 551–556.—The method is based upon pptn. of Na as the Na salt of α-methoxyphenylacetic acid (*cf.* Reeve and Christoffel, *Anal. Abstr.*, 1957, **4**, 2087; Reeve, *Ibid.*, 1960, **7**, 24).

H. F. W. KIRKPATRICK

4898. **Rubeanic acid [dithio-oxamide] for determination of copper in human serum.** D. S. McCann, P. Burcar and A. J. Boyle (Dept. of Chem., Wayne State Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 547–548.—*Procedure*—To 2 ml of serum add 4 ml of digestion mixture (72% $HClO_4$ - conc. HNO_3) (1:9) and place the tube in an aluminium heating block at approx. 120°. Switch the hot-plate to high and evaporate the sample mixture to incipient dryness (about 3 hr., with a final temp. of 260° to 290°). Remove the tube, cool, and wash down the side of the tube with 1 ml of malonic acid soln. (10 g in 100 ml of H_2O, neutralised with aq. NH_3 and diluted to 500 ml with H_2O); warm the tube momentarily in boiling H_2O to ensure complete dissolution of the residue. Cool, add 3 ml of buffer - colour reagent and mix, and after 30 min. read the extinction at 385 mμ. Prepare a standard curve for the range 0 to 8 μg of Cu by using the digestion procedure. *Buffer - colour reagent*—Dissolve 300 g of Na acetate trihydrate in 500 ml of H_2O, filter, and to the filtrate add 280 ml of glacial acetic acid. Dissolve 200 mg of gum acacia in 20 ml of H_2O, and 100 mg of dithio-oxamide in 20 ml of ethanol, warming if necessary. Mix the three soln. and dilute to 1 litre. This reagent is stable for months if stored in a refrigerator.

H. F. W. KIRKPATRICK

4899. **Spectrophotometric determination of serum copper with oxalylhydrazide.** E. W. Rice (Pittsburgh Univ. Med. Sch., Pa., U.S.A.). *J. Lab. Clin. Med.*, 1960, **55** (2), 325–328.—*Procedure*—To serum or heparinised plasma (1·0 ml) in a test-tube (13 mm × 100 mm) add 0·70 ml of 2 *N* HCl containing 0·1% of oxalylhydrazide. Mix and allow to stand for 10 min. Add 1·0 ml of 20% (w/v) trichloroacetic acid, stir well, cover the tube with Parafilm, set aside for 5 min. then centrifuge for 15 min. Treat two water blanks and a standard (2·0 μg of Cu per ml) similarly. Transfer 2·0 ml of clear liquid from the blanks, sample and standard to test-tubes containing a pinch of citric acid crystals, agitate to dissolve, and to one blank add a pinch of EDTA (disodium salt). Add to all tubes 0·50 ml of aq. NH_3 (sp. gr. 0·90) and 0·50 ml of cold 50% (v/v) aq. acetaldehyde soln., mix and measure the colour at 542 mμ after 30 min. against the blank containing EDTA. Calibration is rectilinear with up to 5 μg of Cu per 3 ml of final solution. The mean recovery of Cu is 95% and the standard deviation of a single determination is 2·7 μg of Cu per ml. Results agree well with those obtained by a standard colorimetric method. Tissue and urine can be assayed after wet oxidation.

W. H. C. SHAW

4900. **Determination of metals in blood serum by atomic absorption spectroscopy. I. Calcium.** J. B. Willis (Div. of Chem. Phys., C.S.I.R.O., Chem. Res. Lab., Melbourne, Australia). *Spectrochim. Acta*, 1960, **16** (3), 259–272.—The apparatus previously described (Box and Walsh, *Ibid.*, 1960, **16**, 255) is used with an air - acetylene flame. The variable effect of the protein content of serum samples is eliminated by its prior removal by coagulation and centrifuging. The effect may be considerably reduced, and the determinations made much more quickly, by direct measurements on serum diluted with a 1% soln. of EDTA (disodium salt). Calcium contents obtained by atomic absorption methods are significantly higher than those obtained by the standard oxalate - permanganate procedure, which is considered to give low results. Replicate determinations (7) on a single sample gave a coeff. of variation of 1%.

II. Magnesium. J. B. Willis. *Ibid.*, 1960, **16** (3), 273–278.—By using an air - acetylene flame, as little as 0·05 ml of serum can be analysed after dilution with a 1% soln. of EDTA or $SrCl_2$, which eliminate the effect of variable protein content. Other metals and phosphorus have no effect on the absorption measurements, which can be made quickly and accurately.

P. T. BEALE

4901. **X-ray spectroscopy in the clinical laboratory. I. Calcium and potassium.** S. Natelson, M. R. Richelson, B. Sheid and S. L. Bender (Roosevelt Hosp., West 59th St., New York, U.S.A.). *Clin. Chem.*, 1959, **5** (6), 519–531.—Serum is applied to filter-paper, and the air-dried spot is exposed to an X-ray field. The soft X-rays emanating from the sample are collimated to a LiF flat crystal. The beam is then passed through a second collimator to the detector, a gas flow counter, attached to conventional counting and recording equipment. Directions and precautions for operating the Norelco standard X-ray spectrograph are given.

H. F. W. KIRKPATRICK

4902. **Simplified colorimetric method for determination of mercury in biologic materials.** D. L. Sorby and E. M. Plein (Univ. of Washington, College of Pharmacy, Seattle). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (3), 160–162.—Digest the sample (1 g) with conc. H_2SO_4 and 50% H_2O_2 soln. according to the method of Polley and Miller (*cf. Anal. Abstr.*, 1955, **2**, 3420), then mix an aliquot containing between 10 and 25 μg of Hg with 0·25 *N* HCl (50 ml) and a 0·0004% soln. of dithizone in $CHCl_3$ (25 ml), shake thoroughly and measure the extinction of the lower layer at 400 mμ. The max. error is ±5%.

A. R. ROGERS

4903. **Combined use of ion exchangers for the pre-treatment of serum for the determination of aluminium with Eriochrome cyanine R.** M. Seibold (I Med. Klin. d. Univ. München). *Z. anal. Chem.*, 1960, **173** (5), 388–394.—Of the cations present in human serum, only Fe, Cu and Mn interfere seriously in the determination of Al, and these can be removed as anionic chloride complexes on Dowex 1-X10. Phosphate is also eliminated, and recovery of Al is quant. *Procedure*—Ash the dried serum at 550°, dissolve the residue in HCl, dry and re-ash. Dissolve the residue in 5 ml of H_2O acidified with 2 drops of 10 *N* HCl and transfer with H_2O to a column of cation-exchange resin (Dowex 50-X8). Allow to run through (5 to 10 drops per min.) and reject the percolate. Elute the cations on to a column of Dowex 1-X10 with 10 *N* HCl (6 × 5 ml). Evaporate the percolate, dissolve the residue in 5 ml of 0·2 *N* HCl and treat with 1·5 ml of an aged 0·1% soln. of Eriochrome cyanine R (C. I. Mordant Blue 3). Titrate with 2 *N* NaOH from yellow to violet, then with 0·2 *N* acetic acid to yellow - orange. Add 15 ml of buffer soln. (14·2 g of Na acetate and 1·74 g of acetic acid in 1 litre of H_2O) and dilute to 25 ml with H_2O. After 20 hr. in the dark at const. temp. [not stated] measure the extinction at 534 mμ. The relative precision is 1·3 to 5·2% for 1 to 2 μg of Al.

P. D. PARR-RICHARD

4904. **Determination of aluminium in blood serum with ion-exchange resins and Eriochrome cyanine R.** M. Seibold (1 Med. Klinik, Univ. München, Germany). *Klin. Wochschr.*, 1960, **38** (3), 117–119.—Blood serum is dried and ashed, and interfering ions are separated by a mixture of anion- and cation-exchange resins. The Al is then determined colorimetrically with Eriochrome cyanine R (C.I. Mordant Blue 3). The method is applicable to the range 5 to 50 μg of Al per 100 ml of serum.

H. F. W. KIRKPATRICK

4905. **Determination of vanadium in urine.** Z. Bartošová (Dept. Ind. Diseases, KÚNZ, Ostrava, Czechoslovakia). *Pracovní Lékařství*, 1959, **11** (10), 518–521.—The method based on the catalytic action of vanadium on the oxidation of the organic chromogen with $KClO_3$ and the reaction with *p*-aminodiethylaniline (**I**) (Rockhold and Talvitie, *Anal. Abstr.*, 1957, **4**, 1915) was used for the control of the vanadium content in urine. *Procedure*—Dilute 1 ml of the urine to 11 ml with H_2O, add a satd. soln. of $KClO_3$ (1 ml) and a soln. of **I** (1%) in glacial acetic acid, mix and heat for 15 min. in a water bath. Cool quickly and measure the colour at 540 mμ. Make a blank determination and compare with a calibration curve prepared by the addition of 0 to 1 μg of V to the sample of urine.

J. ZÝKA

4906. **Determination of radioactive sulphur in biological materials.** H. Jeffay, F. O. Olubajo and W. R. Jewell (Dept. of Biochem., Coll. of Med., Univ. of Illinois, Chicago, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 306–308.—*Procedure*—Heat the sample (0·25 g of tissue or 0·5 ml of serum or urine) to 270° with 0·5 or 1 ml of a modified Pirie reagent [saturate 1 vol. of a mixture of conc. HNO_3 and 60% $HClO_4$ (3:1) with $Mg(NO_3)_2$ and add 3 vol. of the acid mixture] until a dry residue is obtained. If oxidation is incomplete, cool, add more reagent and re-heat. Cool the residue to 150° and dissolve it in glycerol (1 ml) previously heated to 100°. Cool the soln., add a mixture of absolute ethanol - dimethylformamide (1:3) (6 ml) with shaking, then add 10 ml of a toluene soln. containing 0·3% of 2:5-diphenyloxazole and 0·01% of 1:4-di-(5-phenyloxazol-2-yl)benzene in diffused light, cool at 3° for 1 hr. and count in a liquid scintillation counter. The counting efficiency is $\simeq$49%. Non-radioactive materials present in the sample do not interfere.

A. R. ROGERS

4907. **Serum iron determination using direct colour extraction.** J. Fischl (Chem. Lab., "Assaf Harofe" Gov. Hosp., Zrifin, Israel). *Clin. Chim. Acta*, 1960, **5** (2), 164–170.—*Procedure*—To 1 ml of serum in a 15-ml centrifuge tube add 1 ml of H_2O and 0·2 ml of 100% (w/v) trichloroacetic acid soln. Mix, place in a boiling-water bath for 15 min., shaking at 5-min. intervals, then remove and allow to cool. Add 1 drop of 30% H_2O_2 and 3 ml of colour reagent (30 g of KSCN dissolved in 100 ml of 4% acetone mixed with 500 ml of *iso*butyl alcohol; this should be colourless; discard if not water-clear). Mix by vigorous shaking and centrifuge at 3000 r.p.m. for 10 min. To 2 ml of the supernatant liquid add 2 drops of propane-1:2-diol, mix and read the extinction (R_1) with a green filter against unused colour reagent. Add 3 to 5 mg of ascorbic acid, mix well, allow to stand for 20 min. and read again (R_2). Treat 2 ml of H_2O for the blank (B), and 0·1 ml of standard soln. (containing 1 μg of Fe) mixed with 1·9 ml of H_2O for the standard (S) by the same procedure. Then μg of Fe per 100 ml of serum $= 100[R_1 - (B + R_2)/(S - B)]$.

H. F. W. KIRKPATRICK

4908. **Determination and identification of cyanide in biological material.** S. L. Tompsett (Northern Gen. Hosp., Edinburgh, Scotland). *Clin. Chem.*, 1959, **5** (6), 587–591.—Distillation is carried out from a 100-ml round-bottomed flask attached to a water-cooled condenser, with all-glass connections. To 20 ml of aq. soln. add one of the following: (*a*) 2 ml of 10 *N* HCl, (*b*) 1 g of buffer salt mixture, pH 6·5 (2 parts of KH_2PO_4 and 1 part of Na_2HPO_4), (*c*) 1 g of $NaHCO_3$. Distil into 1 ml of 10 *N* NaOH, collecting a total of 10 ml of distillate. To the distillate add glacial acetic acid (1 ml), Br water (1 ml) and As_2O_3 soln. (2% aq. soln. prepared by boiling under a reflux condenser) (1 ml) in that order in rapid succession, mixing after each addition. Add benzidine - pyridine reagent (5 ml), dilute to 25 ml with H_2O and read against a blank at 520 mμ after 15 min. Prepare standards containing 5, 10 and 25 μg of HCN similarly. The benzidine - pyridine reagent is freshly prepared from (*i*) 5 g of benzidine dihydrochloride dissolved in 100 ml of 0·1 *N* HCl, and (*ii*) 60 ml of pyridine diluted to 100 ml with H_2O and 10 ml of 10 *N* HCl added, by mixing 5 ml of (*i*) with 25 ml of (*ii*). The Br water is prepared by diluting a conc. soln. with H_2O until no blue colour is produced with the reagent. Variation in the proportion of the theoretical yield of HCN in the distillates from soln. of different pH serves for differentiation.

H. F. W. KIRKPATRICK

4909. **Determination of ethanol in blood by means of gas chromatography.** B. Chundela and J. Janák (Lab. of Toxicol. and Forensic Chem., Charles' Univ., Prague). *Čas. Lék. Čes.*, 1960, **99** (3–4), 90–95.—The determination was simplified by the use of hydrophilic stationary phases (*e.g.*, diglycerol or Carbowax) on Sterchamol together with an internal standard of a volatile compound (*e.g.*, *n*-butanol or ethyl methyl ketone). The sample (0·10 ml for thermal-conductivity detection or 0·02 ml for ionisation detection) is placed directly on the column. A sensitivity of 0·1% with a relative error of $\pm$5% for 0·8 to 1·9% of ethanol was achieved.

J. ZÝKA

4910. **Amperometric determination of penicillin in urine.** J. Grafnetterová (Inst. for Med. Postgraduation, Prague). *Čas. Lék. Čes.*, 1960, **99** (3–4), 182–185.—The method is based on the alkaline hydrolysis of penicillin to penicillamine and amperometric titration of the SH group with $HgCl_2$ soln. *Procedure*—Extract urine (5 ml) for 1 min. with glycine buffer soln. (pH 1·93) (5 ml) and $CHCl_3$ (25 ml). Discard the aq. layer and dry the $CHCl_3$ layer with anhyd. Na_2SO_4 (1·5 g). Transfer 20 ml of the $CHCl_3$ extract to a test-tube containing freshly prepared 2% $NaHCO_3$ soln. (5 ml), shake for 1 min., transfer 3 ml of the aq. layer to another tube, add 0·1 *N* NaOH, mix and set aside for 30 min. Add *N* HCl (1 ml) and heat in a boiling-water bath for 1 hr. Cool, dilute to 5 ml, mix, transfer 1 ml to a vessel containing borate buffer soln. (pH 9·23) and titrate amperometrically (rotating platinum electrode - S.C.E.) with 0·001 *N* $HgCl_2$, without the use of applied voltage.

J. ZÝKA

4911. **Scheme for the rapid identification in urine of commonly used sedatives, hypnotics and tranquillisers.** G. Sobelewski and G. Nadeau (Hôp.

Saint-Michel Archange, Quebec, Canada). *Clin. Chem.*, 1960, **6** (2), 153–161.—Group separation is carried out as follows. Urine (10 ml) is acidified with HCl (1 ml) and extracted with benzene (10 ml). The benzene is tested for glutethimide. The aq. soln. is extracted with *iso*butyl alcohol (2 × 10 ml) and the organic phase is examined in u.v. light; a yellowish-green fluorescence indicates reserpine and its analogues. The *iso*butyl alcohol extract is then shaken with H_2O (10 ml) containing *N* NaOH (1 ml). The organic phase is tested for phenothiazines. The aq. phase is neutralised with *N* HCl (1 ml), buffered with satd. KH_2PO_4 soln. (2 ml) and extracted with ethyl ether (15 ml). The ether extract is tested for barbiturates. The aq. soln. from the *iso*butyl alcohol extraction is adjusted to a pH of 9 to 10 and extracted with ethyl acetate (10 ml). The ester soln. will contain opium alkaloids and some incompletely extracted phenothiazines. Another aliquot of urine is made alkaline with *N* NaOH (1 ml) and extracted with ethyl ether (10 ml). The ether soln. is tested for meprobamate. Bromide may be detected in the aq. layer. Suitable tests are described and discussed.

H. F. W. KIRKPATRICK

4912. **Method for the routine determination of chlorpropamide in plasma.** R. H. Carmichael (Lilly Lab. for Clin. Res., Marion County Gen. Hosp., Indianapolis, Ind., U.S.A.). *Clin. Chem.*, 1959, **5** (6), 597–602.—To serum or plasma (0·5 ml) in a glass-stoppered centrifuge tube add 0·02 *N* HCl (2·5 ml) and *iso*amyl acetate (10 ml), stopper tightly, mix by inversion for 10 min. and centrifuge. Transfer 6·0 ml of the ester layer to a 15-ml graduated centrifuge tube, add 0·1% 1-fluoro-2·4-dinitrobenzene soln. in *iso*amyl acetate (1·0 ml), cover the mouth of the tube with a glass marble to prevent excessive evaporation and heat at 125° for 10 min. Allow to stand at room temp. for 30 min., make up the vol. if necessary to 7 ml, and read at 346 mμ against a blank prepared from plasma treated as above without the colour reagent. Standards containing 1 to 10 μg of chlorpropamide per ml in the ester are assayed similarly.

H. F. W. KIRKPATRICK

4913. **Determination of acetazolamide in human urine using a diazotisation and coupling procedure.** W. Harke, C. Schirren and R. Wehrmann (Univ.-Hautklinik, Hamburg-Eppendorf, Germany). *Klin. Wochschr.*, 1959, **37** (19), 1040–1044.—The method described is an adaptation of the method for sulphonamides. The urine is heated under reflux with HCl to free the acetylated amino group and this is diazotised with $NaNO_2$ and HCl and coupled with thymol in alkaline soln. The colour produced is measured at 546 mμ. H. F. W. KIRKPATRICK

4914. **Determination of 4-allyl-*NN*-diethyl-2-methoxyphenoxyacetamide in human material.** H. Simmer, I. Simmer and H. Beck (Univ.-frauenklinik, Freiburg i. Br.). *Arzneimittel-Forsch.*, 1960, **10** (3), 153–156.—The method of Pulver (*Anaesthetist*, 1957, **6**, 167) involving hydrolysis and colorimetric determination of the resulting ethylamine with CS_2 (Dowden, *Biochem. J.*, 1938, **32**, 455), gave low values for 4-allyl-NN-diethyl-2-methoxyphenoxyacetamide (**I**) in blood and placentae. Higher recoveries were obtained by the extraction of **I** into ethyl ether instead of ethanol, but recoveries from placentae were still low. Metabolites of **I** in blood were determined satisfactorily after further extraction into ethanol, but erroneous results were obtained with urine, amniotic liquor or placentae. Quaternary ammonium compounds interfered. A u.v. spectrophotometric method is described, comprising purification by extraction into various solvents, paper chromatography with *n*-heptane, elution, measurement of the extinction of the eluate at 255, 278 and 300 mμ, and application of an Allen correction; 5 μg of **I** may be detected. Mean recoveries from blood and placentae were 96 and 81%, respectively. The coeff. of variation (10 duplicates) were ±3% and ±6%, respectively.

A. G. COOPER

4915. **Sensitive procedure for urinary *p*-nitrophenol determination as a measure of exposure to parathion.** J. W. Elliott, K. C. Walker, A. E. Penick and W. F. Durham (Communicable Disease Center, Bureau of State Services, U.S. Dept. of Health, Education, and Welfare, Wenatchee, Washington). *J. Agric. Food Chem.*, 1960, **8** (2), 111–113.—Not less than 10 μg of *p*-nitrophenol is determined in a sample of ⩾100 ml of urine by hydrolysis with HCl to liberate conjugated *p*-nitrophenol, extraction successively into ethyl ether - benzene (1:4), 20% NaOH soln. and methyl cyanide, reduction to *p*-aminophenol, and colorimetric measurement at 620 mμ as indophenol blue. The recovery of *p*-nitrophenol is 70 to 75%. The method is as rapid as, and more sensitive than, determinations of blood cholinesterase for measuring the absorption of parathion. M. D. ANDERSON

4916. **Determination of glucose in blood serum by a new rapid and specific automatic system.** H. V. Malmstadt and G. P. Hicks (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 394–398.—The method is based on the coupled enzyme reaction in which the oxidation of glucose is specifically catalysed by glucose oxidase to form H_2O_2, which reacts with *o*-dianisidine in the presence of horseradish peroxidase to form a coloured product. A few seconds after the commencement, the rate of development of colour is directly proportional to the glucose concn. The instrument described automatically measures this rate within ≃1 min. of the beginning of the reaction. The results for glucose in blood serum show a coefficient of variation of ±2%; recovery is quant. The serum must be deproteinised manually before the sample is supplied to the instrument.

A. R. ROGERS

4917. **Rapid photometric method for the determination of apparent glucose in blood.** E. Valverde. *An. Asoc. Quim. Argentina*, 1959, **47** (2), 135–142.—The method is a modification of the alkaline ferricyanide method of Hagedorn and Jensen, employing photometric measurement of the iodine liberated from KI by the excess of ferricyanide. *Procedure*—The blood sample is cleared with cold Folin and Wu's tungstate reagent and a portion of the cleared sample (2 ml, equivalent to 0·2 ml of blood) is heated for 10 min. in a boiling-water bath with 4 ml of 0·005 *N* alkaline $K_3Fe(CN)_6$, containing 10·6 g of Na_2CO_3 per litre. After cooling the sample, 3 ml of KI soln. and 3 ml of 3% acetic acid are added, the mixture is shaken, then centrifuged, and the extinction is measured at 420 mμ. The KI soln. is prepared by mixing equal vol. of soln. of $ZnSO_4 \cdot 7H_2O$ (10 g) and NaCl (25 g) per 100 ml and KI (5 g) and NaCl (25 g) per 100 ml. A calibration graph is prepared by treating glucose standards in a similar manner. Fasting values are from 80 to 130 mg of apparent glucose per 100 ml of blood, and the reproducibility is ±2%. E. C. APLING

4918. **Glucose determination by automatic chemical analysis.** H. J. Grady and M. A. Lamar (Dept. of Med., Univ. of Kansas Med. Centre, Kansas City, U.S.A.). *Clin. Chem.*, 1959, **5** (6), 542–550.—Stabilisation of the temp. of the dialysing unit increases the accuracy of the automatic method by Hoffman's procedure (*Amer. J. Med. Tech.*, 1958, **24**, 271). H. F. W. KIRKPATRICK

4919. **Organic analysis. XXIII. Determination of blood sugar and urine sugar with 3:6-dinitrophthalic acid.** Tsutomu Momose, Akira Inaba, Yoshiko Mukai and Mitsuko Watanabe (Pharm. Inst., Univ. Kyushu, Fukuoka, Japan). *Talanta*, 1960, **4** (1), 33–37.—Reducing sugars heated with 3:6-dinitrophthalic acid (**I**) give a red colour stable in the presence of $Na_2S_2O_3$, and 20 or 100 μg of glucose per ml can be determined by this method at 450 mμ with an accuracy within ± 5 or $\pm 2{\cdot}5\%$, respectively. The method is suitable for routine determinations of blood sugar and sugar in urine. *Procedure*—Haemolyse 0·1 ml of blood with 3·5 ml of water and de-proteinise with 5% $Ba(OH)_2.8H_2O$ soln. (0·2 ml) and then with 5% $ZnSO_4.7H_2O$ soln. (0·2 ml). Centrifuge. To the supernatant liquid (2 ml) or to the urine sample (2 ml) add 0·2% aq. **I** soln. (1 ml) and then 1 ml of a soln. containing 20% of Na_2CO_3 and 5% of $Na_2S_2O_3.5H_2O$. Heat the mixture in a boiling-water bath for 10 min. exactly, cool in running water for 3 min., and dilute to 20 ml. Read the extinction at 450 mμ against a reagent blank and obtain the sugar content from a calibration curve. J. P. STERN

4920. **Fluorimetric determination of acetone in urine.** I. Hynie, B. Večerek and J. Wagner (Inst. Med. Chem., Charles' Univ., Prague). *Čas. Lék. Čes.*, 1960, **99** (3–4), 88–90.—*Procedure*—Mix the sample (25 ml) with 50% H_2SO_4 (10 ml) and distil off the acetone with steam. Transfer the distillate (10 to 12 ml) to a 25-ml flask containing 0·35 *N* NaOH (10 ml), add a 0·025% methanolic soln. of 2-naphthol (1 ml) and dilute to vol. with H_2O. Measure the fluorescence, carry out a blank and compare with a calibration curve. The mean error is $\pm 3\%$. Acetaldehyde ($> 0{\cdot}1\%$) does not interfere. J. ZÝKA

4921. **Simple method for the determination of blood urea nitrogen with special reference to automatic chemical analysis.** H. J. Richter and Y. S. Lapointe (Ottawa Civic Hosp., Ontario, Canada). *Clin. Chem.*, 1959, **5** (6), 617–620.—A modified diacetyl monoxime method is described. H. F. W. KIRKPATRICK

4922. **Determination of 5-hydroxyindol-3-ylacetic acid in urine.** H. Schön, W. Ordnung and E. Schmidt. *Klin. Wochschr.*, 1960, **38** (8), 405–406.—The method of Udenfriend is modified. *Procedure*—Acidify a 24-hr. specimen of urine with 5 ml of conc. HCl. Shake 20 ml with 5 ml of 2:4-dinitrophenylhydrazine soln. (0·3% in 2 *N* HCl) for 15 min. Add 20 ml of ethyl acetate (**I**), shake for 10 min., separate the aq. layer and re-extract with **I**. Unite the **I** extracts, dry with anhydrous Na_2SO_4 and pass them through a column 2·5 cm in diameter containing 5 g of acid Al_2O_3 (Brockmann). Wash the column with **I** (3 × 10 ml) and shake the eluate with 5 ml of 0·33 *M* phosphate buffer soln. (pH 8) for 15 min. To 4 ml of the buffer phase add 1 ml of 1-nitroso-2-naphthol soln. (0·1% in ethanol) and 1 ml of $NaNO_2$ reagent (25 ml of 2 *N* H_2SO_4 and 1 ml of 2·5% $NaNO_2$ soln., freshly mixed) and incubate at 37° for 5 min. Extract the buffer soln. with **I** (2 × 5 ml), reject the **I** extracts, and measure the extinction of the aq. soln. at 540 mμ. Evaluate from a standard curve. H. F. W. KIRKPATRICK

4923. **Colorimetric method for measuring indican [in urine].** A. M. Marko and F. B. Reynolds (Dept. of Biochem. and Paediatrics, Univ. Saskatchewan, Saskatoon). *Canad. J. Biochem. Physiol.*, 1960, **38** (3), 253–262.—Urine (1·0 or 2·0 ml) is passed through a column of charcoal (20 mm) supported by glass wool in a tube 150 mm × 9 mm. (The charcoal is prepared by deactivating with palmitic acid and treating with 0·5 *N* NaOH, followed by repeated washing with water.) After washing the column with water (2 × 1·0 ml), the aromatic compounds are eluted with 0·7 *M* phenol (3 × 2·0 ml) and the eluate is collected in a 10-ml flask, and made up to vol. with water. To an aliquot (1·0 ml) of the eluate is added 3% *p*-dimethylaminobenzaldehyde soln. in 6 *N* HCl (1·0 ml) followed, after 30 min. at room temp., by 2 *M* Na acetate in 50% ethanol (10·0 ml). The extinction is then read at 520 mμ. A standard curve is prepared by treating aq. indican soln. (1·0 ml, containing 0 to 50 μg) with the *p*-dimethylaminobenzaldehyde and Na acetate soln. A survey of the literature on the determination of indican and indigoid pigments is presented. (51 references.) R. A. BRENAN

4924. **Procedures for testing urine specimens dried on filter-paper.** H. K. Berry (Children's Hosp. Res. Foundn, Univ. Cincinatti, Ohio, U.S.A.). *Clin. Chem.*, 1959, **5** (6), 603–608.—Paper spot-tests are described for phenylpyruvic acid, sugars, protein and chondroitinsulphuric acid. Paper-chromatographic identification of phenylalanine, *o*-hydroxyphenylacetic acid, glucose and lactose is also described. H. F. W. KIRKPATRICK

4925. **New methods for the quantitative estimation of myo-inositol.** E. L. Kean and F. C. Charalampous (Pennsylvania Univ., Philadelphia, U.S.A.). *Biochim. Biophys. Acta*, 1959, **36** (1), 1–3.—Two methods requiring the use of rat-kidney enzyme are given. In one, the amount of glucuronate formed from inositol is determined colorimetrically by the orcinol method and, in the other, the rate of oxidation of reduced triphosphopyridine nucleotide in the presence of glucuronate is followed spectroscopically at 340 mμ. W. H. C. SHAW

4926. **Determination of neuraminic (sialic) acid, glucose and fructose in spinal fluid.** N. M. Papadopoulos and W. C. Hess (Georgetown Univ. Med. Sch., Washington, D.C., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **88** (1), 167–171.—In the method described, sialic acids are determined colorimetrically in spinal fluid (0·5 ml) with an orcinol - HCl - $FeCl_3$ reagent against N-acetylneuraminic acid as standard. The extinction at 570 mμ is proportional to concn. up to 80 μg of standard. The same weights of fructose and glucose give about 76 and 3%, respectively, of the colour. Fructose is determined colorimetrically on a further 0·5 ml of sample with a resorcinol reagent, and glucose on 0·1 ml by a glucose oxidase - peroxidase - *o*-dianisidine method. Corrections are then made for the effect of these on the orcinol colour. The method can be used for the determination of total, free and bound sialic acids, and gives results in good agreement with those obtained by an ion-exchange procedure. W. H. C. SHAW

4927. **Thiobarbituric acid spray reagent for deoxy sugars and sialic acids.** L. Warren (Nat. Inst. of Arthritis and Metab. Dis., Bethesda, Md., U.S.A.). *Nature*, 1960, **186**, 237.—To detect deoxy sugars and 2-oxo-3-deoxygluconic acid the solvent-free paper is sprayed with aq. 0·02 *M* $NaIO_4$. After 15 min. the paper is sprayed with ethanediol - acetone - conc. H_2SO_4 (50:50:0·3), and after 10 min. with a 6% aq. soln. of Na 2-thiobarbiturate. Red spots appear after heating at 100° for 5 min. which show red fluorescence under u.v. light. For sialic acids 0·05 *M* $NaIO_4$ in 0·05 *N* H_2SO_4 is used, the ethanediol and thiobarbituric acid soln. being the same. A heating time of 10 min. is necessary.
H. F. W. KIRKPATRICK

4928. **Micro-determination of carbohydrates and proteins.** G. Halliwell (Dept. of Enzymol., Rowett Res. Inst., Bucksburn, Aberdeen, Scotland). *Biochem. J.*, 1960, **74** (3), 457–562.—An iodimetric micro-method is described. The carbohydrate or protein is oxidised with $K_2Cr_2O_7$ in 97% H_2SO_4, and the excess of the reagent is determined colorimetrically after the addition of CdI_2 - starch soln., the intensity of the blue colour being measured with a photoelectric absorptiometer. The amounts of glucose, cellobiose, sucrose, and starch can be ascertained from a calibration graph for glucose. The method is applicable to the determination of 9 to 40 μg of carbohydrate or protein in 0·45 ml of soln.; the recovery for carbohydrates is 96 to 101%. A sub-micro method for 0·9 to 4 μg of carbohydrate, and a modification for 100 to 700 μg, are also described. The oxidation of carbohydrates is rapid and is complete in 7 min. at 95° to 100°; proteins require 20 min. at this temp. The method is recommended for the determination of micro quantities of carbohydrates, proteins, and their breakdown products formed enzymically or otherwise, for following the purity of enzymes or proteins during fractionation procedures, and for the analysis of chromatographic eluates. J. N. ASHLEY

4929. **Separation of phosphate esters by paper chromatography.** D. A. Rappoport and P. T. Chen (Baylor Univ. Med. Coll., Houston, Texas, U.S.A.). *Biochim. Biophys. Acta*, 1960, **38** (1), 156–157.—De-proteinised tissue extracts are treated with Dowex-50 ion-exchange resin (H^+ form) and then applied to Whatman 41 H paper for ascending development with ethyl acetate - acetic acid - water (3:3:1) for 15 hr. After drying, the chromatograms are developed by the descending technique in the second dimension with ethyl methyl ketone - 2-methoxyethanol (7:2) purified by passage through Dowex-50 resin (H^+ form) and then diluted with 0·7 part of conc. aq. NH_3 and 2·3 parts of water Development is for 22 hr., after which the carbohydrate phosphates are detected by two spray-reagents or (for ^{32}P derivatives) by an autoradiographic technique. W. H. C. SHAW

4930. **Paper chromatography of heparin and related sulphated mucopolysaccharides.** L. Spolter and W. Marx (S. California Univ., Los Angeles, U.S.A.). *Biochim. Biophys. Acta*, 1960, **38** (1), 123–129.—Chromatography of 30 μg of material is carried out by the descending technique on Whatman No. 1 paper for 12 hr. at 26° ± 2° after equilibration for 3 to 4 hr. with 0·04 *M* ammonium formate (pH 4·3) and *iso*propyl alcohol (13:7). Separation of heparin (R_F, 0·57) from chondroitin sulphate (solvent front) is attained. A study is made of the constituents of heparin from various sources and of the effects of different proportions of solvents on the separations. The loss of resolution of beef heparin constituents observed on "aged" filter-paper could be restored by changing the solvent mixture to 7:3. W. H. C. SHAW

4931. **Rapid method for the separation of plasmals.** R. W. Keenan and B. H. Marks (Ohio State Univ., Columbus, U.S.A.). *Biochim. Biophys. Acta*, 1960, **39** (3), 533–535.—Paper chromatography of long-chain (C_{14} to C_{18}) aldehydes as the 2:4-dinitrophenylhydrazones is carried out on Whatman No. 3 paper treated with a 2% solution of soft paraffin in light petroleum (boiling-range 65° to 110°) and dried. Ascending development is carried out with methanol - water (24:1) for 4 hr. The spots are located under long-wave u.v. light, cut out, eluted with 2 ml of CCl_4 and the extinction is measured at 345 mμ. The amounts required are 12 to 14 μg of each derivative, but 2 to 3 μg is sufficient for identification. Methods for preparing tissue extracts and the derivatives are given. W. H. C. SHAW

4932. **Structure of plasmalogens. IV. Lipids in normal and neoplastic tissues of man and in normal tissues of rabbit and rat. [Determination of plasmalogen.]** M. M. Rapport and B. Lerner (N.Y. State Dept. of Health, Albany). *Biochim. Biophys. Acta*, 1959, **33**, 319–325.—Total lipid extracts of tissues were analysed for plasmalogen content by two independent methods: formation of the aldehyde *p*-nitrophenylhydrazone and addition of iodine under conditions specific for αβ-unsaturated ethers. The results agreed, with a mean variation of <10%. CHEM. ABSTR.

4933. **Potentiometric iodimetric determination of plasmalogen.** W. T. Norton (Yeshiva Univ., New York, U.S.A.). *Biochim. Biophys. Acta*, 1960, **38** (2), 340–342.—The method of Rapport and Lerner (*Anal. Abstr.*, 1960, **7**, 4932) is modified by substituting potentiometric titration of the excess of iodine with aq. $Na_2S_2O_3$ soln. for the visual end-point. Smaller samples may be used and higher accuracy, particularly on coloured samples, is achieved. W. H. C. SHAW

4934. **Method for determining the concentration of ubiquinone in mitochondrial preparations.** A. M. Pumphrey and E. R. Redfearn (Dept. of Biochem., Univ., Liverpool 3, England). *Biochem. J.*, 1960, **76** (1), 61–64.—The method consists essentially of (*a*) the simultaneous termination of any enzymic reaction and denaturation of enzyme proteins with methanol - pyrogallol; this does not destroy the ubiquinone or alter the oxidation - reduction state of ubiquinone - ubiquinol mixtures; (*b*) extraction of the lipids with light petroleum; (*c*) removal of interfering lipids, such as phospholipids, by partitioning the lipid between light petroleum and methanol, and (*d*) spectrophotometric determination of the ubiquinone by the standard method which involves measurement of the extinction at 275 mμ and, after reduction to the ubiquinol, at 290 mμ.
J. N. ASHLEY

4935. **Spectrophotometric behaviour of azobilirubin and azotaurobilirubin.** M. Jirsa and V. Jirsová (Med. Clinic, Charles' Univ., Prague, Czechoslovakia). *Clin. Chem.*, 1959, **5** (6), 532–541 (in English).—Extinction and absorption maximum values are influenced by pH, alcohol and albumin.

The determination of direct bilirubin by the Malloy and Evelyn procedure is subject to error, and a revision of colorimetric methods for this estimation is needed. H. F. W. KIRKPATRICK

4936. **Direct chromatography of serum lipids without solvent extraction.** G. V. Marinetti and E. Stotz (Rochester Univ. Med. Sch., N.Y., U.S.A.). *Biochim. Biophys. Acta*, 1960, **37** (3), 571–573.—Ascending chromatography of serum (10 to 20 μl) is carried out on paper impregnated with silicic acid for 4 to 5 hr. at 23° with di*iso*butyl ketone - acetic acid - water (40:20:3) for the separation of phosphatides. Non-phosphatides (cholesterol, cholesteryl esters, glycerides and fatty acids) are separated with *n*-heptane - di*iso*butyl ketone (16:1) during 1 to 1·25 hr. The air-dry chromatograms are stained with Rhodamine 6G (C.I. Basic Red 1).
W. H. C. SHAW

4937 **Determination of de-esterified fatty acids in blood serum with special reference to the hydroxamic acid method.** H. Weller (I Med. Klinik, Freien Univ., Berlin, Germany). *Klin. Wochschr.*, 1959, **37** (18), 951–957.—The method used is a modification of that of Bauer and Hirsch (*Arch. Biochem.*, 1949, **20**, 242). An alcohol - ether extract of the serum is evaporated to dryness, the residue is dissolved in absolute H_2O-free ether and treated in the cold with Na ethoxide and hydroxyammonium chloride soln. for a short reaction time. The solvent is removed, the residue is treated with a ferric perchlorate - perchloric acid reagent and the colour is read at 530 mμ. The results compare favourably with those of the gravimetric method.
H. F. W. KIRKPATRICK

4938. **Symposium on catecholamines.** *Pharmacol. Rev.*, 1959, **11**.—The following papers are of analytical interest. **Points to be considered in running chromatograms of tissue extracts,** M. Vogt, pp. 249–251. **Survey of chemical and physical methods for measuring catecholamines,** S. Udenfriend, pp. 252–255. **Fluorescence and its measurement,** R. L. Bowman, pp. 256–261. **Development and application of the trihydroxyindole method for catecholamines,** U. S. von Euler, pp. 262–268. **Techniques to improve the specificity of the trihydroxyindole procedure,** G. Cohen, pp. 269–272. **Estimation of adrenaline and noradrenaline concentrations in human plasma by the trihydroxyindole method,** H. L. Price, pp. 273–275. **A simple technique involving solvent extraction for estimation of noradrenaline and adrenaline in tissues,** P. A. Shore, pp. 276–277. **Fluorimetric estimation of catechol compounds by the ethylenediamine condensation method,** H. Weil-Malherbe, pp. 278–288. **Suitability of the ethylenediamine method of Weil-Malherbe and Bone and modifications for quantitating plasma pressor amines,** W. M. Manger, pp. 289–295. **Some spectrophotofluorimetric observations on blood and urine catecholamine assays,** J. R. Crout, pp. 296–299. **Detection and assay of 4-(2-aminoethyl)-catechol (dopamine),** A. Carlsson, pp. 300–304.

4939. **Simple and rapid determination of small amounts of adenine.** J. S. Knypl and R. Antoszewski (Dept. of Plant Physiol., Univ. of Łódź, Poland). *Anal. Chim. Acta*, 1960, **22** (3), 297–298 (in English).—Adenine (3 to 10 μg) in aq. soln. can be determined by applying it to Whatman No. 1 paper impregnated with Ag_3AsO_4. The spot is made visible with Ilford ID2 photographic developer, and fixed with acid fixing soln., and its area is compared with those of a series of standards. The results are accurate to within $\simeq \pm 5\%$.
W. T. CARTER

4940. **Studies on synovial tissue. VII. [Determination of] concentrations of creatine and phosphocreatine in synovial tissue.** E. R. Cook, D. P. P. Thomas and J. T. Dingle (M.R.C., Rheumatism Res. Unit, Manor Hosp., Bath, Somerset, England). *Biochem. J.*, 1960, **76** (1), 120–124.—Ennor and Rosenberg's method (*Biochem. J.*, 1952, **51**, 606) in which an alkaline soln. of diacetyl and 1-napththol is used to determine creatine, before and after hydrolysis, the difference representing phosphocreatine, is simplified and modified so as to be applicable to various tissues, including human and rabbit synovial tissue. The cells are ruptured by a soln. that contains Tween 80, EDTA, *p*-chloromercuribenzoic acid, and alkali. Sliced soft tissues yield 97% of their creatine, but synovial tissues are more resistant and the average extraction is only 87%. J. N. ASHLEY

4941. **Determination of carnitine in biological media.** G. Deltour, J. Broekhuysen and L. Dierickx (Services des Recherches, Soc. des Lab. Labaz, Brussels, Belgium). *Clin. Chim. Acta*, 1960, **5** (2), 181–185.—A method is described for the separation of carnitine from interfering substances by paper electrophoresis for determination by the method of Friedman (*Arch. Biochem. Biophys.*, 1958, **75**, 24).
H. F. W. KIRKPATRICK

4942. **Organic chemical microscopy. VII. Amino acids and their dibenzofuran-2-sulphonates in qualitative organic analyses.** R. E. Dunbar and F. J. Ferrin (N. Dakota State Coll., Fargo, U.S.A.). *Microchem. J.*, 1960, **4** (1), 59–72.—The microscopical appearance of the salts of amino acids with dibenzofuran-2-sulphonic acid is quite distinctive in most cases and can be used as a means of identification, particularly when m.p. are not conclusive. The salts are easily prepared by the addition of dibenzofuran-2-sulphonic acid soln. to a soln. of the amino acid or its hydrochloride; the salts are insoluble in water and are easily purified. Many of the derivatives have relatively high m.p., but these are sufficiently sharp to be useful for identification. Although decomposition occurs in many cases, the m.p. of the salts appear to be more reliable and reproducible than those of the parent acids. Soln. of the derivatives in alcohol can be titrated with alcoholic KOH to give significant neutralisation equivalents, which provide an excellent means of identification. (30 photomicrographs.)
G. P. COOK

4943. **Paper-chromatographic analysis of acids (horizontal migration method). Separation and identification of amino-acid mixtures.** V. K. Mohan Rao (Lucknow Univ.). *J. Sci. Ind. Res., B, India*, 1960, **19** (2), 62–66.—The paper-chromatographic behaviour of amino acids in the presence of halogen acids and salts has been studied. The R_F values of amino acids are influenced by the nature and concn. of the salt present in the solvent rather than in the soln. to be chromatographed. The presence of salt prevents the streaking of arginine and lysine halogen acid salts and lowers the R_F values of amino acids at higher concn. O. M. WHITTON

4944. **Paper-chromatographic differentiation between α-monoamino acids and other ninhydrin-positive substances.** P. O. Larsen and A. Kjær

(Royal Vet. and Agric. Coll., Copenhagen, Denmark). *Biochim. Biophys. Acta*, 1960, **38** (1), 148–150.—Dried chromatograms are dipped in a solution containing 0·25% of $Cu(NO_3)_2.3H_2O$ and 2% of anhydrous sodium acetate in methanol and dried for 2 min. at 70°. After dipping the chromatograms in a 0·2% solution of ninhydrin in acetone they are air-dried for 1 min. and then heated at 70° for 40 to 50 sec. α-Monoamino acids do not react, or appear as faint spots only. The reactions of 50 amino acids and related compounds are tabulated.

W. H. C. SHAW

4945. **The separation of metabolic products into fractions by paper chromatography.** R. Ya. Shkol'nic and N. G. Doman (Inst. Biochem., Acad. Sci., Moscow). *Biokhimiya*, 1960, **25** (2), 276–281.—Amino acids and sugars are separated from organophosphorus compounds by means of the solvent *n*-propanol - conc. aq. NH_3 - 0·5% EDTA (disodium salt) (6:3:1). Mixtures of amino acids and sugars are completely separated into fractions by treating the chromatograms with a solvent consisting of pyridine - acetone - *n*-propanol - conc. aq. NH_3 - 0·5% EDTA (disodium salt) (60:10:18:9:3) or pyridine - *n*-propanol - conc. aq. NH_3 - 0·5% EDTA (disodium salt) (15:6:3:1). Details are also given of mixtures of conc. aq. NH_3 with methanol, ethanol, *n*-butanol and pyridine as solvents for the separation of organophosphorus compounds and organic acids from amino acids and sugars.

A. BURWOOD-SMITH

4946. **Observations on the use of copper salts in the spectrophotometric determination of amino acids.** G. Cuzzocrea and G. Lamonica (Ist. Biochim. Appl., Univ. Messina, Italy). *Biochim. Appl.*, 1960, **7** (2), 96–101.—A modification of the method of Spies (*J. Biol. Chem.*, 1952, **195**, 65), giving improved sensitivity, is described. A soln. of the sample, containing from 5 to 50 μg of amino acid per ml, is incubated for 2 hr. at 20° with 4 volumes of a satd. soln. of copper carbonate in borate buffer (pH 8·7); the extinction is measured at 230 mμ, and, when necessary, the extinction due to the amino acid itself is deducted. Molar extinction coeff. for the copper complexes of 16 amino acids are tabulated.

E. C. APLING

4947. **Quantitative method for the differential determination of hydroxylamine and β-aspartyl hydroxamate in mixtures.** J. Yashphe, Y. S. Halpern and N. Grossowicz (Dept. of Bacteriology, Hebrew Univ., Hadassaj Med. School, Jerusalem, Israel). *Anal. Chem.*, 1960, **32** (4), 518–520.—The method is based on the fact that hydroxylamine (**I**) is oxidised to nitrite by iodine and therefore gives a colour reaction with sulphanilic acid and l-naphthylamine at pH values of 2·3 and 3·7, while β-aspartyl hydroxamate (**II**) is oxidised only at pH 3·7. To the sample (1 ml) is added Na acetate soln. (5%) (5 ml), sulphanilic acid reagent (10 g per litre of 30% acetic acid) (1 ml) and iodine soln. (1·3 g per 100 ml of glacial acetic acid) (0·5 ml). The mixture is shaken and allowed to stand for 3 to 5 min., and excess of iodine is removed with $Na_2S_2O_3$ soln. (2·5%) (0·5 ml). After addition of conc. HCl (0·5 ml), the colour is developed with l-naphthylamine soln. (3 g per litre of 30% acetic acid) (1 ml), the total volume is made up to 10 ml, and after 20 min. the extinction is measured at 530 mμ. The whole procedure is then repeated with the replacement of 5% Na acetate soln. by 0·1 *M* acetate buffer (pH 3·6). The colour intensity obtained in the first measurement represents the amount of **I** present, and that in the second the total amount of **I** and **II**. The amount of **II** is calculated by difference after reference to calibration curves. Similar results have been obtained with other hydroxamates. The method is recommended for use with biological systems in which **I** and hydroxamates may be formed as intermediates.

S. M. MARSH

4948. **Colorimetric determination, without previous isolation, of glutamic acid in hydrolysates of nutrients.** H. Zimmermann (Max Planck Inst. f. Ernährungsphysiol., Dortmund, Germany). *Z. Lebensmitt-Untersuch.*, 1960, **112** (1), 46–49.—The application of the method (described) used by Sachs and Brand (*J. Amer. Chem. Soc.*, 1954, **76**, 3601) to various amino-acid mixtures with or without glutamic acid (**I**) is examined. The extinction values (E) for mixtures of animal origin without **I** are sufficiently uniform and (in comparison with the values given by **I**) small to warrant the use of a linear graph from E = 0·033 for 0% to E = 0·55 for 100% of **I** for the determination of **I** within ±2% in soln. containing 15 to 20 mg of amino acids, the concn. of the acids being determined as N × 6·25. The results obtained for plant hydrolysates are subject to a constant deduction of 0·6% (total N × 6·25 = 100%) to allow for the coloration given by γ-aminobutyric acid. Allowance must also be made for the possible presence in samples of substances giving a coloration with hydroxylamine and $FeCl_3$ without previous treatment with HNO_2. Formulae for the calculation of results are also given.

P. S. ARUP

4949. **Chromatographic purity of amino acids: arginine.** M. S. Dunn and E. A. Murphy (Chem. Lab., Univ. of Calif., Los Angeles, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 461–463.—The R_F values of 29 amino acids after single, double and triple development in one or two dimensions with three solvent systems are tabulated. The method is used for detecting amino-acid impurities in standard samples of arginine. Suitable colour tests for detecting as little as 0·1 to 0·2% of impurity in 500 μg of L-arginine hydrochloride are tabulated.

H. F. W. KIRKPATRICK

4950. **Determination of arginine released in human blood plasma after plasminogen activation. Use of a cation-exchange resin.** S. I. Cohen (Harvard Med. Sch., Mass., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **86** (2), 166–168.—After plasminogen activation of the prepared plasma with streptokinase, unbound arginine is adsorbed on a column of Dowex 50-X8 ion-exchange resin (Na^+ form). The column is then washed with 0·05 *M* NaCl and eluted with 1·25 *M* NaOH. Arginine in the eluate is then determined colorimetrically with a modified 1-naphthol - urea (Sakaguchi) reagent.

W. H. C. SHAW

4951. **Modified method for hydroxyproline determination.** F. Hutterer and E. J. Singer (Mt. Sinai Hosp., New York, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 556–558.—The method is designed to eliminate errors due to instability of the specific chromogen, impurity of the *p*-dimethylaminobenzaldehyde (**I**), incomplete removal of H_2O_2, and loss of reaction specificity in the presence of tissue compounds. For the purification of **I**, 100 g is dissolved in ethanol (200 ml) at 70°, charcoal is added and after heating for 5 min. and stirring the soln. is filtered. **I** is pptd. by adding excess of H_2O, then filtered off,

washed with H_2O and dried *in vacuo*. This procedure is repeated until a white product is obtained that gives a colourless soln. in *n*-propanol. A 5% soln. in this solvent is prepared. *Recommended procedure*—To 1 ml of a soln. containing 1 to 10 μg of hydroxyproline in a suction tube add 0·2 ml of 0·05 *M* $CuSO_4.5H_2O$, 0·5 ml of 2·5 *N* NaOH and 0·5 ml of 4% H_2O_2 (standardised against $KMnO_4$). Shake, set aside at room temp. for 5 min., then place in a water bath at 70° for 10 min. After the first 5 min. apply vacuum and agitate the tube for 30 sec. to complete the removal of H_2O_2. Cool in ice, add 0·8 ml of 8 *N* H_2SO_4 and 2·5 ml of **I** soln. Shake vigorously, place in a water bath at 70° for 40 min., then cool, and read the extinction at 560 mμ.

H. F. W. KIRKPATRICK

4952. **Identification and quantitative estimation of ethanolamine and serine in lipid hydrolysates.** W. L. Magee, R. W. R. Baker and R. H. S. Thompson (Guy's Hosp. Med. Sch., London, England). *Biochim. Biophys. Acta*, 1960, **40** (1), 118–123.—Chromatography of 20 to 60-μl portions of the prepared extract containing 0·01 to 0·10 μmole of ethanolamine or serine is carried out on Whatman 3 MM paper developed by the ascending technique for 2 to 4 hr. with ethyl methyl ketone - 2-methoxyethanol - 20% acetic acid (8:3:4). The air-dry chromatograms are dipped in a ninhydrin - $SnCl_2$ reagent and, after heating at 50° for 90 min., the coloured areas are cut out, eluted with 50% aq. ethanol and, after filtration, the extinction is measured at 570 mμ. Standards are chromatographed similarly. The results are compared with those given by a fluorodinitrobenzene method and the differences are discussed. Methods for the preparation of extracts and for the hydrolysis are given.

W. H. C. SHAW

4953. **Determination of cystine by its catalytic effect on the iodine - azide reaction.** R. D. Strickland, P. A. Mack and W. A. Childs (Res. Div,. Veterans Admin. Hospital, Albuquerque, N. Mex., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 430–436.—*Procedure*—Mix the sample (0·5 ml of neutralised protein hydrolysate, containing 0·5 to 5 μg of cystine) with iodine - azide reagent [mix 2 *M* sodium azide (50 ml) with 0·065 *M* KI_3 (20 ml), adjust to pH 5·8 and dilute with H_2O to 100 ml] (5 ml) and set aside for 30 to 60 min. Extract the liberated iodine from a 0·5-ml aliquot by shaking with H_2O (5 ml) and CCl_4 (5 ml) and measure the extinction of the lower layer at 525 mμ. Prepare also reagent blanks and standards and calculate by means of a calibration curve. The results agree with those by the gravimetric method of Evans (*Arch. Biochem.*, 1945, **7**, 439) but are lower than those by a modified Folin method (Block *et al.*, *J. Biol. Chem.*, 1940, **134**, 567) which was found to be subject to interference by materials present in the hydrolysates. The theory of the reaction, and its application to other compounds containing bivalent sulphur are discussed.

A. R. ROGERS

4954. **Quantitative determination of 5-hydroxytryptophan, 5-hydroxytryptamine and 5-hydroxyindolylacetic acid by paper chromatography.** A. Carcasona, F. Unterharnscheidt and J. Cervos-Navarro (Inst. of Neuropath., Univ., Bonn, Germany). *Klin. Wochschr.*, 1959, **37** (14), 761–763.—Suitable solvent systems and colour reagents for the separation and determination of these substances are given. R_F values of each substance in the solvent systems used are tabulated.

H. F. W. KIRKPATRICK

4955. **Protein determination on the basis of copper-binding capacity.** J. Westle,/ and J. Lambeth (Chicago Univ., Ill., U.S.A.). *Biochim. Biophys. Acta*, 1960, **40** (2), 364–366.—In the method described, the protein solution, previously purified by dialysis, or a suspension of the trichloroacetic acid-pptd. proteins containing 0·05 to 1·0 mg of protein is treated with an alkaline Cu^{2+} reagent. After allowing to stand, excess of Cu^{2+} is removed by the addition of a suspension of Dowex-1 ion-exchange resin (Cl^- form) and then of a sodium diethyldithiocarbamate reagent containing bovine serum albumin as complex-stabiliser. After centrifugation, the extinction of the supernatant liquid is measured at 446 or 486 mμ according to concn. Calibration is rectilinear with up to 0·4 mg of protein.

W. H. C. SHAW

4956. **Rapid screening method for the elimination of cross-contamination in the determination of protein-bound iodine.** J. A. Ackerman and J. T. Myers (Bendinger & Schlesinger Lab., 47 Third Ave., New York, U.S.A.). *Clin. Chem.*, 1959, **5** (6), 615–616.—To 0·1 ml of 4 *N* Na_2CO_3 in a test-tube (100 mm × 15 mm) add 0·1 ml of serum and place in a boiling-water bath for 3 min. To the cooled soln. add 2 ml of *N* HCl. Shake gently, avoiding breaking up the protein clot, remove the clot with a glass rod and add 0·1 ml of 0·1 *N* sodium arsenite followed by 0·4 ml of 0·02 *N* ceric ammonium sulphate. Any serum showing decolorisation within 10 min. is eliminated as contaminated. Normally the yellow colour persists for more than 30 min.

H. F. W. KIRKPATRICK

4957. **Improved protein resolution of concentrated tissue extract in zonal column electrophoresis.** S. Sorof, E. M. Young, M. M. Spence and P. L. Fetterman (Inst. Cancer Res., Philadelphia, Pa., U.S.A.). *Biochim. Biophys. Acta*, 1960, **38** (3), 559–561.—In a modification of the method described by Porath (*Doct. Diss., Uppsala Univ.*, 1957) for zonal electrophoresis of proteins in vertical columns of ethanolysed cellulose, the columns are closed with membranes of regenerated cellulose. Improved resolution and better control of the separations are attained.

W. H. C. SHAW

4958. **Use of diethylaminoethylcellulose in the separation of proteins from egg-white and other biological materials.** S. Mandeles (West. Reg. Res. Lab., Albany, Calif., U.S.A.). *J. Chromatography*, 1960, **3** (3), 256–264 (in English).—Procedures are given for the separation and analysis of proteins in egg-white, the livetin fraction of egg yolk, chicken-breast muscle extract, cabbage extract, and extracts of *Escherichia coli* by gradient elution after adsorption on a column (40 cm × 2·5 cm) of washed diethylaminoethylcellulose. Elutions are accomplished by changing the molar composition (0·02 to 0·1) of glycine - phosphate buffer added to the column from time to time. The course of the elution is followed by measuring the extinction of the fractions at 280 mμ, although modification of the elution schedule is best determined by continuous instrumental measurement of the extinction, at 254 mμ, of the eluate. The method gives higher resolution than does electrophoretic analysis, *e.g.*,

12 components of egg-white were identified and 9 from the livetin fraction. Some limitations of the procedure are discussed. W. J. BAKER

4959. **Fluorimetric micro-determination of human serum albumin.** J. J. Betheil (Dept. of Biochem., Albert Einstein Coll. of Med., Yeshiva Univ., New York, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 560–563. —Interaction of serum albumin in alkaline soln. with Vasoflavine (a sulphonated, methylated benzothiazole derivative), a commercially available dye, yields an increase in fluorescence in linear relation with the albumin concn. The reaction is extremely sensitive and specific and the albumin in a 5-μl sample of serum can be accurately determined.
H. F. W. KIRKPATRICK

4960. **Albumin - globulin ratio in serum. A comparison of salt fractionation and protein paper electrophoresis.** W. B. Yeoman (Frenchay Hosp., Bristol, England). *Clin. Chem.*, 1960, **6** (2), 122–129.—The efficiency of salt fractionation is tested by paper electrophoresis of the concentrated filtrate. Total pptn. of globulins is effected by 27·2% Na_2SO_4 soln. H. F. W. KIRKPATRICK

4961. **Procedure for the determination of cerebrospinal fluid total protein and gamma-globulin in neurological disorders.** N. M. Papadopoulos, W. C. Hess, D. O'Doherty and J. E. McLane (Dept. of Biol. Chem., Georgetown Univ., Washington, D.C., U.S.A.). *Clin. Chem.*, 1959, **5** (6), 569–574.—Determination of both total protein and γ-globulin by one method is necessary in obtaining a significant ratio of their concn. in c.s.f. *Total protein*—Dilute 0·4 ml of c.s.f. to 2 ml with 1·25% Na_2CO_3 soln., add 2 ml of 0·05% $CuSO_4.5H_2O$ soln. and 5 ml of 12·5% Na_2CO_3 soln., mixing after each addition. Add 1 ml of Folin - Ciocalteau phenol reagent (diluted 1 to 5 with H_2O), mix well and allow to stand for 15 min. at room temp. Read at 540 mμ and obtain the protein from a standard curve. *γ-Globulin*—To 2 ml of c.s.f. in a 15-ml centrifuge tube add 2 ml of $ZnSO_4$ reagent (dissolve 3·60 g of barbitone and 1·50 g of Na barbitone in H_2O, add 1·75 g of $ZnSO_4.7H_2O$, dissolve, and make up to 1 litre with H_2O), shake well and place in a refrigerator overnight. Centrifuge, decant the fluid, dissolve the ppt. in 2 ml of 1·25% Na_2CO_3 soln. and proceed as for total protein. In control patients the γ-globulin was 8·3% (mean) s.d. $\pm$2·0, in multiple sclerosis 30·0%, s.d. $\pm$3·0, and in other neurological diseases 17·0%, s.d. $\pm$2·3 of the total protein. The test is useful as an aid in the diagnosis of multiple sclerosis.
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W. H. C. Shaw

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H. F. W. Kirkpatrick

4972. **New colour reaction for the quantitation of serum cholesterol.** R. L. Searcy and L. M. Bergquist (Los Angeles County Osteopathic Hosp., Calif., U.S.A.). *Clin. Chim. Acta*, 1960, **5** (2), 192–199.—An orange colour is given by cholesterol in $FeSO_4$ - glacial acetic acid soln. when conc. H_2SO_4 is added. The reaction is applied directly to an acetone - ethanol extract of serum. *Procedure for total cholesterol*—Add 0·1 ml of serum to 0·9 ml of acetone - abs. ethanol (1:1), mix well and centrifuge. To 0·4 ml of the clear supernatant soln. add 6 ml of a satd. soln. of $FeSO_4.7H_2O$ in glacial acetic acid, followed by 2 ml of conc. H_2SO_4 introduced into the mixture with force so as to cause immediate mixing. After 10 min. measure the colour at 490 mμ against a blank prepared with 0·4 ml of solvent alone. Free cholesterol may be determined by digitonin pptn. A standard curve is employed for evaluation.

H. F. W. Kirkpatrick

4973. **Rapid semi-micro procedure for estimating free and total cholesterol.** A. J. Courchaine, W. H. Miller and D. B. Stein, jun. (Thomas M. Fitzgerald Mercy Hosp., Darby, Pa., U.S.A.). *Clin. Chem.*, 1959, **5** (6), 609–614.—The method is a modification of those of Zlatkis *et al.* (*J. Lab. Clin. Med.*, 1953, **41**, 486) and Zak *et al.* (*Amer. J. Clin. Path.*, 1954, **24**, 1307) in which a $FeCl_3$ reagent is used.

H. F. W. Kirkpatrick

4974. **Sulphosalicylic acid as a substitute for toluene-*p*-sulphonic acid in the estimation of cholesterol.** F. Rappaport and F. Eichhorn (Beilinson Hosp., Petah Tikwa, Israel). *Clin. Chim. Acta*, 1960, **5** (2), 161–163.—The method of Pearson *et al.* (*Brit. Abstr. C*, 1953, 474) is reviewed and an improved method in which sulphosalicylic acid is used is described.

H. F. W. Kirkpatrick

4975. **Fluorimetric determination of phenolic steroids in acid medium.** R. Scholler, J. Longchampt and M. F. Jayle (École de Puériculture, Fac. de Méd., 26 Bd. Brune, Paris, France). *Bull. Soc. Chim. France*, 1960, (2), 189–202.—The literature of the excitation of fluorescence in H_2SO_4 soln. of phenolic steroids is reviewed and a modification of the Lérès type T 2D spectrophotometer for fluorimetry is described. *Procedure*—The soln. containing the steroids is evaporated to dryness and heated for 10 min. at 100° with 2 ml of 15 *M* H_2SO_4, then cooled. The fluorescence is excited by the 435·8-mμ Hg line or a band around 455 mμ from a xenon lamp. The fluorescence is measured at 479 mμ for oestrone and oestriol and at 474 mμ for 17β-oestradiol. The methyl esters of oestrone and 17β-oestradiol have fluorescence intensities close to that of these phenolic steroids themselves, though with max. slightly displaced to longer wavelengths. The absorption, fluorescence and excitation spectra of a number of phenolic steroids are measured to establish the optimum conditions, and the effects of concn. of H_2SO_4 and time and temp. of heating, and of self-absorption are studied. There is a rectilinear relationship between intensity of fluorescence and weight of steroid between 1 and 4 μg of oestrone, oestriol or 17β-oestradiol. Non-phenolic steroids give a fluorescence <3·2% of that of oestrone; the value for tetrahydrocortisone, however, rises to 7·7%.

E. J. H. Birch

4976. **Determination of 3β-hydroxysterols with anthrone reagent.** G. V. Vahouny, R. M. Mayer, J. H. Roe and C. R. Treadwell (George Washington Univ. Med. Sch., Washington, D.C., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **86** (2), 210–214.—Free 3β-hydroxysterols are determined by pptn. of the extracted total sterols with digitonin. The centrifuged ppt. is washed with hot aq. acetone to remove excess of digitonin and the sterol digitonides are then determined, with cholesterol digitonide as standard, by the anthrone reaction, with a reagent stabilised (2 to 4 weeks) by the addition of 3% of thiourea. Total 3β-hydroxysterols are similarly determined after saponification of the sample. The specificity and precision of the method are discussed.

W. H. C. Shaw

4977. **Spectrophotometric studies of the Zimmermann reaction.** H. S. Friedmann (Med. Lab. Centre, 7520th USAF Hosp., Middx., England). *Clin. Chem.*, 1959, **5** (6), 575–586.—The effects of reagent concn., time and temp. have been investigated. *Procedure*—Evaporate aliquots of the extract dissolved in CCl_4 to dryness in cuvettes, add 0·4 ml of *m*-dinitrobenzene (0·1% in absolute ethanol) and 0·4 ml of 2·5 *N* KOH in 80% ethanol (1 vol. of 12·5 *N* KOH added to 4 vol. of absolute ethanol immediately before use). Maintain at 0°

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4971. **Paper chromatography of steroids. A systematic approach using a generalised R_M function.** P. Kabasakalian and A. Basch (Chem. Res. and Development Div., Schering Corp., Bloomfield, N. J., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 458–461.—The work of Brooks *et al.* (*J. Chem. Soc.*, 1957, 1175) is extended to cover several solvent systems and to enable the R_F value of a steroid in each system to be calculated from its structure. Values of ΔR_M for substituent groups are derived from experiments with a pregnane series, and the method is evaluated by application to a related series of steroids.

H. F. W. KIRKPATRICK

4972. **New colour reaction for the quantitation of serum cholesterol.** R. L. Searcy and L. M. Bergquist (Los Angeles County Osteopathic Hosp., Calif., U.S.A.). *Clin. Chim. Acta*, 1960, **5** (2), 192–199.—An orange colour is given by cholesterol in $FeSO_4$ - glacial acetic acid soln. when conc. H_2SO_4 is added. The reaction is applied directly to an acetone - ethanol extract of serum. *Procedure for total cholesterol*—Add 0·1 ml of serum to 0·9 ml of acetone - abs. ethanol (1:1), mix well and centrifuge. To 0·4 ml of the clear supernatant soln. add 6 ml of a satd. soln. of $FeSO_4.7H_2O$ in glacial acetic acid, followed by 2 ml of conc. H_2SO_4 introduced into the mixture with force so as to cause immediate mixing. After 10 min. measure the colour at 490 mμ against a blank prepared with 0·4 ml of solvent alone. Free cholesterol may be determined by digitonin pptn. A standard curve is employed for evaluation.

H. F. W. KIRKPATRICK

4973. **Rapid semi-micro procedure for estimating free and total cholesterol.** A. J. Courchaine, W. H. Miller and D. B. Stein, jun. (Thomas M. Fitzgerald Mercy Hosp., Darby, Pa., U.S.A.). *Clin. Chem.*, 1959, **5** (6), 609–614.—The method is a modification of those of Zlatkis *et al.* (*J. Lab. Clin. Med.*, 1953, **41**, 486) and Zak *et al.* (*Amer. J. Clin. Path.*, 1954, **24**, 1307) in which a $FeCl_3$ reagent is used.

H. F. W. KIRKPATRICK

4974. **Sulphosalicylic acid as a substitute for toluene-*p*-sulphonic acid in the estimation of cholesterol.** F. Rappaport and F. Eichhorn (Beilinson Hosp., Petah Tikwa, Israel). *Clin. Chim. Acta*, 1960, **5** (2), 161–163.—The method of Pearson *et al.* (*Brit. Abstr. C*, 1953, 474) is reviewed and an improved method in which sulphosalicylic acid is used is described.

H. F. W. KIRKPATRICK

4975. **Fluorimetric determination of phenolic steroids in acid medium.** R. Scholler, J. Longchampt and M. F. Jayle (École de Puériculture, Fac. de Méd., 26 Bd. Brune, Paris, France). *Bull. Soc. Chim. France*, 1960, (2), 189–202.—The literature of the excitation of fluorescence in H_2SO_4 soln. of phenolic steroids is reviewed and a modification of the Lérès type T 2D spectrophotometer for fluorimetry is described. *Procedure*—The soln. containing the steroids is evaporated to dryness and heated for 10 min. at 100° with 2 ml of 15 *M* H_2SO_4, then cooled. The fluorescence is excited by the 435·8-mμ Hg line or a band around 455 mμ from a xenon lamp. The fluorescence is measured at 479 mμ for oestrone and oestriol and at 474 mμ for 17β-oestradiol. The methyl esters of oestrone and 17β-oestradiol have fluorescence intensities close to that of these phenolic steroids themselves, though with max. slightly displaced to longer wavelengths. The absorption, fluorescence and excitation spectra of a number of phenolic steroids are measured to establish the optimum conditions, and the effects of concn. of H_2SO_4 and time and temp. of heating, and of self-absorption are studied. There is a rectilinear relationship between intensity of fluorescence and weight of steroid between 1 and 4 μg of oestrone, oestriol or 17β-oestradiol. Non-phenolic steroids give a fluorescence <3·2% of that of oestrone; the value for tetrahydrocortisone, however, rises to 7·7%.

E. J. H. BIRCH

4976. **Determination of 3β-hydroxysterols with anthrone reagent.** G. V. Vahouny, R. M. Mayer, J. H. Roe and C. R. Treadwell (George Washington Univ. Med. Sch., Washington, D.C., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **86** (2), 210–214.—Free 3β-hydroxysterols are determined by pptn. of the extracted total sterols with digitonin. The centrifuged ppt. is washed with hot aq. acetone to remove excess of digitonin and the sterol digitonides are then determined, with cholesterol digitonide as standard, by the anthrone reaction, with a reagent stabilised (2 to 4 weeks) by the addition of 3% of thiourea. Total 3β-hydroxysterols are similarly determined after saponification of the sample. The specificity and precision of the method are discussed.

W. H. C. SHAW

4977. **Spectrophotometric studies of the Zimmermann reaction.** H. S. Friedmann (Med. Lab. Centre, 7520th USAF Hosp., Middx., England). *Clin. Chem.*, 1959, **5** (6), 575–586.—The effects of reagent concn., time and temp. have been investigated. *Procedure*—Evaporate aliquots of the extract dissolved in CCl_4 to dryness in cuvettes, add 0·4 ml of *m*-dinitrobenzene (0·1% in absolute ethanol) and 0·4 ml of 2·5 *N* KOH in 80% ethanol (1 vol. of 12·5 *N* KOH added to 4 vol. of absolute ethanol immediately before use). Maintain at 0°

for 60 min., add 0·8 ml of 95% ethanol to each cuvette, mix by inversion and read at 520 mμ against a reagent blank. This method reduces high blank readings by eliminating the effect of ageing on ethanolic KOH soln. H. F. W. KIRKPATRICK

4978. **Sub-fractionation of human serum enzymes.** C. A. Dubbs, C. Vivonia and J. M. Hilburn (Univ. of California Medical Center, Los Angeles, U.S.A.). *Science*, 1960, **131**, 1529–1531.—Evidence is given for the sub-fractionation of human serum cholinesterase, aromatic esterase and acid phosphatase by starch-gel electrophoresis. Methods are given for localising these sub-fractions with respect to the normal protein zones of the starch-gel pattern (*cf.* Smithies, *Biochem. J.*, 1955, **61**, 629).
R. A. HENDEY

4979. **Effects of the method of tissue preparation on the assay of tissue enzyme activities.** S. L. Bonting and I. M. Rosenthal (Dept. of Biol. Chem., Univ. of Illinois Coll. of Med., Chicago, U.S.A.). *Nature*, 1960, **185**, 686–687.—Five methods of preparation of tissue for enzyme assay were compared by determinations of alkaline phosphatase and lactic dehydrogenase. Freeze-dried tissue sections showed activity of both enzymes 2 to 8 times as great as any other preparation, the next best technique being the freeze-dried homogenate. The results stress the importance of careful standardisation of the method of preparation of the tissue in each comparative enzyme study.
H. F. W. KIRKPATRICK

4980. **Improved spectrophotometric determination of amylase with a new stable starch solution.** E. W. Rice (Dept. of Path., Sch. of Med., Univ., Pittsburgh, Pa., U.S.A.). *Clin. Chem.*, 1959, **5** (6), 592–596.—The starch soln. is stabilised by preparation in saturated sorbic acid soln. The amylase is determined by measurement of the starch - iodide complex at 620 mμ.
H. F. W. KIRKPATRICK

4981. **Micro-method for the determination of plasma amylase.** R. W. Marsters, T. D. Kinney and Ku Yin Lin (Dept. of Path., Cleveland Met. Gen. Hosp., Ohio, U.S.A.). *Clin. Chem.*, 1960, **6** (2), 130–139.—*Procedure*—Place 2 ml of 0·75% soluble starch (Lintner) soln., 2 ml of 0·2 *M* phosphate buffer soln. (pH 7·2) and 1 ml of 0·25 *M* NaCl soln. in each of 3 tubes (duplicates and a control). Incubate at 40° for 5 min. then add 0·02 ml of serum or plasma to the test soln. After exactly 15 min. remove the tubes, add 0·5 g of dry powdered picric acid to each tube, mix and add 0·02 ml of serum to the control. Filter through Whatman No. 2 paper, transfer 1 ml of filtrate to tubes calibrated at 5 ml and place them, together with a blank of 1 ml of satd. picric acid soln. and a standard of 1 ml of glucose soln. (200 mg per litre in satd. picric acid soln.), in a boiling-water bath for 20 min. Cool, make up to 5 ml with H_2O and read against the blank at 540 mμ. The unit of activity is the glucose reducing power expressed in mg per 100 ml of serum. The normal range for humans is 120 to 260 units per 100 ml.
H. F. W. KIRKPATRICK

4982. **Spectrophotometric assay of peptidase activity.** F. Binkley and C. Torres (Emory Univ., Atlanta, Ga., U.S.A.). *Arch. Biochem. Biophys.*, 1960, **86** (2), 201–203.—A solution of leucinamide (0·03 *M*) in 0·2 *M* tri(hydroxymethyl)methylamine at pH 8·0 with the addition of 0·001 *M* Mn^{2+} is used as substrate and the change in extinction at 235 mμ is recorded for 10 to 40 min. The activity is expressed as the change in extinction per min. The method is suitable for the assay of partially purified kidney preparations. W. H. C. SHAW

4983. **Determination of carboxypeptidase in duodenal juice.** W. Rick (Med. Klin., Univ. Giessen, Germany). *Klin. Wochschr.*, 1960, **38** (8), 408–409.—Triethanolamine - HCl buffer soln., (0·05 *M*, pH 7·8) (1·5 ml) is mixed with 0·01 to 0·02 ml of juice or 5 to 75 μg of cryst. enzyme dissolved in 10% aq. LiCl soln. The vol. is made up to 2·5 ml with H_2O and warmed at 37° for 3 min.; 0·2 mg of naphthyloxycarbonylphenylalanine in 0·5 ml of buffer is added and the mixture is incubated at 37° for 1 hr. A cooled aq. soln. of tetrazotised *o*-dianisidine (80 mg per 100 ml) (0·5 ml) is added, the soln. is shaken well and after 3 min. the colour is extracted with 5 ml of ethyl acetate. The ester layer is separated, dried with anhyd. Na_2SO_4 and the extinction is measured at 546 mμ against a blank.
H. F. W. KIRKPATRICK

4984. **Measurement of isocitric dehydrogenase activity in body fluids.** G. N. Bowers, Jun. (Wm. Pepper Lab. of Clin. Med., Philadelphia, Pa., U.S.A.). *Clin. Chem.*, 1959, **5** (6), 509–518.—The method of Wolfson and Williams-Ashman (*Fed. Proc.*, 1957, **16**, 273) is modified to improve accuracy and reduce sample size. Details of the recommended procedure are given. H. F. W. KIRKPATRICK

4985. **Storage of blood samples on kieselguhr and the determination of cholinesterase, alkaline phosphatase and urea.** R. A. Simmonds (Div. of Animal Health and Prod., C.S.I.R.O., Glebe, N.S.W., Australia). *Clin. Chem.*, 1960, **6** (2), 162–167.—*Procedure*—Acid-washed kieselguhr (2·5 to 3 g) is placed in a 7-cm sintered glass funnel of No. 2 or 3 porosity and washed several times with H_2O. It is then suspended in 0·1% gelatin soln. and allowed to settle evenly on the sintered surface and the fluid is removed by suction. The damp cake is cut into small cylindrical tablets with a cork borer and these are dried for 30 min. at 100°. Measured vol. of blood or serum (usually 0·05 ml) are pipetted on to the tablets, which are then dried for 2 to 3 hr. at 20° for enzymes or for 30 min. at 50° for urea. For enzyme determination the tablets can be stored for 6 weeks or more at −15° or for 3 weeks at 4°; at 20° the activity deteriorates rapidly. The tablets are satisfactory for urea determination after storage for at least 2 months at 4° or 20°. Methods are described for the chemical determinations.
H. F. W. KIRKPATRICK

4986. **Determination of mercapto groups in myosin by amperometric titration.** Yu. M. Torchinskiĭ. *Ukr. Biokhim. Zhur.*, 1959, **31** (4), 589–595; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (5), Abstr. No. 5754.—Titration of crude rabbit myosin with $AgNO_3$ yields 78 to 79 μmoles of mercapto groups per g of protein; titration with $HgCl_2$ yields 57 μmoles. De-naturing with urea for 2·5 to 3 hr. at 38° increases the amount of titratable mercapto groups by 9%; this indicates the presence of masked mercapto groups in crude myosin inaccessible to the ions of heavy metals. Treatment of myosin with EDTA does not affect the amount of titratable mercapto groups. Iodoacetate at a concn.

of $1{\cdot}77 \times 10^{-3}$ *M* combines with ≃40% of titratable mercapto groups and at a concn. of 9×10^{-3} with ≃67%. The data are discussed in relation to the significance of mercapto groups and adenosine triphosphate activity. K. R. C.

4987. **Ultra-micro determination of transaminases.** M. Novák, M. Vavrečka and V. Vokáč (Výzk. Ústav Výživy Lidu, Prague). *Čas. Lék. Čes.*, 1960, **99** (5), 152–156.—The method is based on the differential photometric determination of the 2:4-dinitrophenylhydrazone of pyruvic acid in the presence of the 2:4-dinitrophenylhydrazone of α-oxoglutaric acid in an alkaline medium.

J. ZÝKA

4988. **The estimation of quinine oxidase in serum in liver disease.** A. F. K. Buys Ballot and J. B. A. Terlingen (State Hospital, Bergweg, Rotterdam, Netherlands). *Klin. Wochschr.*, 1960, **38** (4), 180.—An investigation into the method of Baier (*Anal. Abstr.*, 1959, **6**, 1494) suggests that the positive reactions are produced by lability of proteins rather than by enzyme activity.

H. F. W. KIRKPATRICK

4989. **The activation of plasminogen by staphylokinase: comparison with streptokinase. [Assay of staphylokinase activity.]** F. M. Davidson (Dept. of Path., Inst. of Orthopaedics, Roy. Nat. Orthopaedic Hosp., Stanmore, Middlesex, England). *Biochem. J.*, 1960, **76** (1), 56–61.—A caseinolytic method is described which depends on the activation of plasminogen by the kinase and the subsequent hydrolysis of casein. Several concn. of the staphylokinase are incubated for 30 min. at 37° with human plasminogen (50×10^{-3} unit) in borate buffer (pH 7·4) (1·1 ml). Soluble casein (4%, w/v) (1 ml) is added and the mixture incubated for a further 30 min. The casein is then pptd. with 10% $HClO_4$ (3 ml) and the extinction at 280 mμ is determined on the digestion mixture. The kinase activity is ascertained by interpolation. A unit of the kinase is that activity which, under specified conditions, gives rise to an increase of 0·300 in the extinction.

J. N. ASHLEY

4990. **Assay procedure for a succinate - neotetrazolium reductase system.** T. F. Slater and D. N. Planterose (Dept. of Biochem., Univ. Coll., Gower St., London, England). *Biochem. J.*, 1960, **74** (3), 591–596.—The enzyme system, which is present in rat liver, kidney and mammary gland, and in mouse liver, oxidises succinate, and by a coupled reaction reduces neotetrazolium chloride to the formazan, which is extracted with ethyl acetate, and the extinction of the coloured soln. is determined spectrophotometrically at 510 mμ. In the presence of added vitamins K_3 and C, the formation of formazan increases proportionately with the amount of tissue added. Conditions are described for the application of the method to 0 to 15 mg of liver homogenate. J. N. ASHLEY

See also Abstracts—**4730**, Organic reductants for determination of P. **4731**, Chromatographic determination of P. **4734**, Separation of inorg. orthophosphate from phosphoric esters. **4735**, Determination of As. **4829**, Colorimetric determination of amines and amino acids. **4942**, Identification of amino acids. **5019**, Ca and Mg in blood plasma. **5082**, Preservation of amino-acid chromatograms. **5106**, Determination of steroid structure.

Pharmaceutical analysis

4991. **Reactions between alkaloids and bismuth iodide. The compounds formed and their analytical application.** M. Bobtelsky and M. M. Cohen (Dept. of Inorg. & Anal. Chem., Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1960, **22** (3), 270–283 (in English).—Heterometric titration curves are presented for nitron, cinchonine, strychnine, sparteine, papaverine, ethacridine lactate, acriflavine, phenanthroline, phenazone and atropine in KI soln. at pH 1, with $Bi(NO_3)_3$ soln. as titrant; 0·5 to 1 mg of an alkaloid can be determined in 15 min. with an error ≯2·5%. Each substance forms several compounds, but for analytical purposes it is only necessary to titrate to the first maximum optical density point. Bismuth (0·3 to 0·5 mg) can also be determined with similar precision by titrating with a standard soln. of alkaloid.

W. T. CARTER

4992. **Behaviour of alkaloid salt solutions on aluminium oxide columns. VIII. Chromatographic determination of the purity of dihydromorphinone hydrochloride, dihydrocodeine hydrogen tartrate, dihydrocodeinone hydrogen tartrate and codeine phosphate.** H. Böhme and H. Hocke (Pharm.-chem. Inst., Univ., Marburg/Lahn). *Arch. Pharm., Berlin*, 1960, **293** (3), 342–356.—Dihydromorphinone hydrochloride (0·15 g) dissolved in 10 ml of aq. acetone (5:1) was passed slowly (2 to 3 ml per min.) through a column of 5 g of alumina ("basic," Woelm) and eluted with the same solvent. The free alkaloid in the eluate (75 ml) was titrated with 0·1 *N* HCl, with bromophenol blue as indicator. Dihydrocodeine and dihydrocodeinone hydrogen tartrates were determined similarly, employing 10 g of "neutral" alumina in aq. acetone (5:4). To determine codeine phosphate, 5 g of "neutral" alumina and a mixed bromophenol blue - methylene blue indicator were employed. A. G. COOPER

4993. **Isolation of ergot alkaloids by cation exchange.** T. Zawisza and L. Kuczyński (Dept. Chem. Technol. of Medicinal Drugs, Med. Acad., Wrocław, Poland). *Acta Polon. Pharm.*, 1960, **17** (2), 117–130.—About 90% of the ergot alkaloids can be isolated from a mixture of powdered undefatted ergot and trichloroethylene acidified with acetic acid by extraction with trichloroethylene. The alkaloids are then removed from the extract (containing 10% of added H_2O) by adsorption on the sulphonic acid exchanger MK2 or Wofatit F. Alkaloids are desorbed with 2 *N* NaCl containing 1% of aq. NH_3, and are removed from the column with acetone. The total ergot alkaloids obtained after evaporation of the acetone are of high purity (>90%). W. B. MIASKOWSKI

4994. **Determination of ergotamine and ergotaminine in drugs.** J. J. A. M. van de Langerijt (Lab. Ned. Apoth., Utrecht, The Netherlands). *Pharm. Weekbl.*, 1960, **95** (5), 133–138.—The composition of the *p*-dimethylaminobenzaldehyde (**I**) reagent generally used in the determination of ergot alkaloids was modified so that more reproducible results were obtained. *Procedure*—Mix the sample tablets containing 1·5 to 2 mg of ergotamine tartrate (**II**) with 5 ml of 1% tartaric acid soln. (**III**). Add 10 ml of ethyl ether and 0·5 g of $NaHCO_3$ and mix with 5 g of Celite 545 (**IV**). Transfer this mixture to a column (length 15 to 20 cm, diam. 2·1 cm)

containing 5 g of **IV** and 5 ml of H_2O. Wash the column with 100 ml of ethyl ether and extract the eluate successively with 25-, 10-, 10- and 5-ml portions of **III**. Combine the extracts and dilute to 50 ml with **III**. Add 6 *N* aq. NH_3 to an aliquot of this soln. containing 1 to 1·5 mg of **II** until the soln. is alkaline, and extract with 4, 3 and 3 ml of $CHCl_3$. Evaporate the combined extracts to 3 ml under a CO_2 or N atmosphere, keeping the temperature below 25°. Add 1·5 g of Celite 545 - formamide (**V**) (mix 15 g of **IV** and 15 g of formamide, add 20 g of **IV** and mix until homogeneous). Remove the $CHCl_3$ in a stream of CO_2 or N. Transfer the mixture to a column containing 15 g of **V** and 30 ml of benzene - light petroleum (9 : 1), saturated with formamide, and remove sufficient solvent mixture to leave about 1 cm above the Celite surface. Transfer 1 g of **V** to the column and add 10 ml of benzene - light petroleum. Wash with benzene - light petroleum at a rate of 60 to 100 drops per min. Confirm by means of u.v. light when the separated fractions of ergotamine and ergotaminine are collected. Dilute each fraction with twice its volume of ethyl ether and extract with **III** so that the soln. obtained contains 10 to 50 μg of ergotamine or ergotaminine per ml. To 2 ml of this soln add 4 ml of **I** (mix 50 ml of H_2O with 53 ml of conc. H_2SO_4, cool and add 500 mg of *p*-dimethylaminobenzaldehyde and 0·4 ml of 10% $FeCl_3.6H_2O$ soln.) and after 10 min. measure the extinction at 550 mμ.

M. J. MAURICE

4995. **Quantitative method for the alkaloid of *Acacia berlandieri*.** B. J. Camp and J. A. Moore (Dept. of Biochem. and Nutrition, Texas Agric. Exp. Sta., College Station). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (3), 158–160.—A colorimetric method is given for the determination of N-methyl-2-phenylethylamine (**I**). The results are accurate within ±10%. *Procedure*—To an ethanolic soln. containing 10 to 100 μg of **I** add 1% ethanolic 1-fluoro-2:4-dinitrobenzene soln. (0·1 ml), 0·2 *M* $NaHCO_3$ (0·2 ml) and abs. ethanol (0·2 ml) and dilute with H_2O to 1·5 ml. Heat in a water bath at 60° for 20 min., add 0·2 *N* NaOH (0·5 ml) and heat for a further 60 min. Dilute to 25 ml, extract with *cyclo*hexane (10 ml) and measure the extinction of the upper layer at 350 mμ against a reagent blank. To determine **I** in the leaves of *A. berlandieri*, extract the air-dried sample with 1% HCl, make alkaline and extract with $CHCl_3$; acidify the $CHCl_3$ extract with ethanolic HCl, evaporate to dryness under reduced pressure, dissolve the residue in abs. ethanol, neutralise and proceed as described above.

A. R. ROGERS

4996. **Spectrophotometric determination of nicotine in tobacco and in tobacco-smoke condensates.** H. Barkemeyer and F. Seehofer (British Amer. Tobacco Co., Hamburg-Bahrenfeld, Germany). *Z. LebensmittUntersuch.*, 1960, **112** (1), 50–52.—This method is based on the observations that the absorption at 259 mμ of acid soln. of nicotine is approx. double that of slightly alkaline soln., and that the background absorption is not affected by changes in pH. Aliquots (2 × 30 ml) of the nicotine steam-distillate (300 ml, collected without acid in the receiver) are diluted to 100 ml, the one with, and the other without, the addition of *N* HCl (10 ml). The difference between the two extinction values × 62·5 gives mg per litre of nicotine in the soln. Results obtained by this method are in considerably closer agreement with gravimetric results than those obtained by the spectrophotometric method of Willits *et al.* (*Anal. Abstr.*, 1954, **1**, 1064).

P. S. ARUP

4997. **Detection and determination of 3:4-benzopyrene and arsenic in cigarette smoke.** J. Pavlů and J. Šula (II Inst. Med. Chem., Charles' Univ., Prague). *Čas. Lék. Čes.*, 1960, **99** (3–4), 101–104.—*Procedure for 3:4-benzopyrene*—Absorb the smoke from 80 to 100 cigarettes in 100 to 200 ml of benzene. Shake thrice with 2 *N* H_2SO_4, thrice with 2 *N* NaOH and thrice with H_2O. Evaporate the dark extract, containing neutral fractions of smoke extracts, to 5 ml and purify chromatographically on a column of Al_2O_3. Elute with benzene and evaporate the eluate to 0·5 ml. Separate chromatographically on acetylated paper by the ascending technique with methanol - ethyl ether - H_2O (4:4:1) as solvent. Extract the spot of 3:4-benzopyrene (violet fluorescence) with benzene (2 × 10 ml), evaporate to 3 ml and determine the fluorescence in a Pulfrich photometer. *Procedure for As*—Absorb the smoke of 20 to 40 cigarettes in 0·03 *N* NaOH and determine the As content colorimetrically with Ag diethyldithiocarbamate after conversion into AsH_3 (Vašák and Šedivec, *Chem. Listy*, 1952, **46**, 341).

J. ZÝKA

4998. **Column-chromatographic method for the determination of digitoxin in digitalis leaves.** F. Neuwald, H.-J. Didier and G. Grimmer (Lab. der Apotheke am Bleck, Bad Bramstedt/Holstein). *Pharm. Acta Helv.*, 1960, **35** (3), 87–95 (in German).—Allow a mixture of the dried coarsely ground leaves and $CaCO_3$ to ferment in water at 37° for 24 hr. Partially purify by pptn. with lead acetate soln., then extract the glycosides with $CHCl_3$. Submit to chromatography on a column of aluminium oxide (activity I); elute successively with benzene - $CHCl_3$ (1:1), light petroleum, H_2O-saturated $CHCl_3$, $CHCl_3$ - methanol (99:1), $CHCl_3$ - methanol (49:1) and methanol. Digitoxin is concentrated into the first few ml eluted by $CHCl_3$ - methanol (49:1), and is determined colorimetrically with xanthhydrol reagent (Pesez, *Ann. Pharm. Franç.*, 1952, **10**, 104).

A. R. ROGERS

4999. **Paper-electrophoretic determination of hydroxymethylanthraquinones in frangula extracts in the presence of phenolphthalein.** M. Sterescu and V. Pelloni (Chem.-Pharm. Res. Inst., București). *Pharm. Zentralh.*, 1960, **99** (3), 121–124.—To determine phenolphthalein in the mixture, submit the untreated sample (10 μl containing ≃40 μg) to electrophoresis on Whatman No. 1 paper in 0·1 *N* NaOH at a potential gradient of 4 V per cm for 3 hr., elute the appropriate zone with 0·1 *N* NaOH (6 ml) and ethanol (2 ml) and measure the extinction of the combined extracts at 530 mμ. To determine hydroxymethylanthraquinones, heat the sample (10 ml containing 1 g of liquid extract of frangula) under reflux for 1 hr. with aq. HCl (*d*, 1·19) (1 ml) and $CHCl_3$ (10 ml), cool, extract the $CHCl_3$ layer with 0·1 *N* NaOH (4 × 5 ml), dilute the combined extracts to 25 ml and submit a 25-μl aliquot to electrophoresis and absorptiometry as described for phenolphthalein. The average error is ≃4%.

A. R. ROGERS

5000. **Paper-chromatographic identification of substances contained in hashish.** F. Korte and H. Sieper (Chem. Inst., Univ. Bonn). *Angew. Chem.*, 1960, **72** (6), 210.—Cannabidiol (**I**), cannabinol (**II**) and tetrahydrocannabinol (**III**) are separated by

reversed-phase descending chromatography with S. & S. paper 2043ahy and the aqueous phase of the solvent system ligroin - benzene - $CHCl_3$ - methanol - water (2:2:1:4:1). The following R_F values were obtained, **I** 0·74, **II** 0·67 and **III** 0·53. Colour reactions with various combinations of spray reagents are tabulated. The determination can be carried out by measuring the u.v. absorption on the chromatogram (*cf.* Korte and Weitkamp, *Anal. Abstr.*, 1959, **6**, 1857), and the wavelengths of max. absorption are given. S. BAAR

5001. **Determination of chloramphenicol.** G. Franchi and C. Pellerano (Ist. Chim. Farm., Siena Univ., Italy). *Ann. Chim., Roma*, 1960, **50** (1–2), 134–139.—The material is allowed to react at room temp. with excess of propionic anhydride in the presence of toluene-*p*-sulphonic acid. Residual anhydride is then estimated by addition of excess of aniline in benzene soln. and titration of the unchanged aniline under anhydrous conditions with $HClO_4$, with crystal violet as indicator, or potentiometrically. The method is applicable to the monoesters of chloramphenicol and various pharmaceutical preparations containing it. L. A. O'NEILL

5002. **Cylinder plate assays for amphotericin B in dosage forms and body fluids.** J. Kramer and A. Kirshbaum (Food Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1960, **10** (3), 188–192.—A description is given of an agar diffusion method for amphotericin B (**I**) in pharmaceutical preparations with *Saccharomyces cerevisiae* as test organism. Samples are diluted with dimethyl sulphoxide and 0·2 *M* phosphate buffer, pH 10·5, to a working range of 0·5 to 2·0 μg per ml. The error with replicate determinations (P = 0·95) is ±10·7%. Amphotericin A at up to five times the concn. of **I** does not interfere. Modifications of the method are described for the detection of minimum concentrations of 0·5 μg per ml in serum and 0·2 μg per ml in urine; the method may also be used for spinal fluid at higher than normal concentrations.

W. H. C. SHAW

5003. **Amperometric titration of phenazone with iodine chloride.** A. I. Gengrinovich, L. E. Korneva and A. M. Murtazaev. *Dokl. Akad. Nauk UzSSR*, 1959, (5), 40–42; *Ref. Zhur., Khim.*, 1960, (7), Abstr. No. 26,411.—A soln. (60 ml) of phenazone (**I**) is titrated amperometrically with 0·01 or 0·001 *N* ICl in 0·4 *N* HCl without an external e.m.f. The cathode is a rotating (600 r.p.m.) platinum microelectrode, and the anode the S.C.E. connected to the cell by an agar bridge with saturated KCl soln. The end of the titration is marked by the rise in current because of discharge of I^+ at the cathode. The reaction is rapid, the titration being completed in 2 or 3 min. The use of **I** to standardise the ICl soln. amperometrically is recommended. The addition of ethanol (one-third of the original vol.) to the soln. allows **I** to be determined in the presence of salicylic acid (**II**) since ethanol reduces the rate of iodination of **II**. The error in determining **I** is 0·1 to 0·5%. C. D. KOPKIN

5004. **Detection and spectrophotometric determination of Novalgin [sodium noramidopyrine methanesulphonate] by means of the sodium salt of 1:2-naphthaquinone-4-sulphonic acid.** E. Maggiorelli and L. Conti (Ist. Chim. Farm. Milit., Italy). *Farmaco, Ed. Prat.*, 1960, **15** (3), 179–183.—The method depends on measurement of the red colour produced by the reaction of Novalgin with sodium 1:2-naphthaquinone-4-sulphonate (**I**). *Procedure*—Dilute the sample (5 ml, containing ≃100 μg of Novalgin) to 50 ml with glacial acetic acid. To an aliquot (5 ml) add a 0·5% soln. of **I** in 50% acetic acid (1 ml) and heat for 20 min. at 60°. Cool to 20° and measure the extinction at 490 mμ. Compare with standards similarly treated. The method is reproducible to within ±5%. Phenazone and amidopyrine do not interfere, but the method is inapplicable in the presence of primary amines. E. C. APLING

5005. **Relationships between the physical-chemical properties and the activity of local anaesthetics. IV. [Determination of cinchocaine and derivatives.]** J. Büchi and X. Perlia (Pharm. Inst., Eidg. Tech. Hochsch., Zürich). *Arzneimittel-Forsch.*, 1960, **10** (4), 297–301.—Absorption spectra and maxima of cinchocaine and its degradation products (2-butoxy- and 2-hydroxy-quinoline-4-carboxylic acid and 2-hydroxyquinoline-4-carboxylic acid diethylethylenediamide) in a buffer soln. of pH 7·4, in 0·1 *N* NaOH and 0·1 *N* HCl are shown. Absorption maxima of 2-alkoxy analogues of cinchocaine are tabulated. These analogues may be determined polarographically by the method of Dusinsky (*Anal. Abstr.*, 1955, **2**, 2538). A. G. COOPER

5006. **Polarographic and photometric determination of 6-mercaptopurine.** J. Vachek (Res. Inst. Pharm. Biochem., Prague). *Českosl. Farm.*, 1960, **9** (3), 126–129.—For the polarographic determination of 6-mercaptopurine (**I**) a medium of McIlvaine buffer soln. (pH 7·1) is recommended, in which a well-developed anodic wave appears ($E_{\frac{1}{2}} = -0{\cdot}26$ V). Hypoxanthine and glucose which interfere in iodimetric and bromatometric titrations do not influence the determination. *Photometric determination*—Dissolve **I** (20 mg) in 0·1 *N* NaOH (100 ml) and dilute 1 to 4 ml of this soln. to 5 ml with 0·1 *N* NaOH; add sodium nitroprusside soln. (2%) (1 ml), set aside for 10 min., add a mixture of anhyd. acetic acid and methanol (4:1) (4 ml) and H_2O (1 ml) and after 5 to 10 min. measure the intensity of the green colour with the use of a red filter. Compare with a calibration curve.

J. ZÝKA

5007. **New colorimetric method for the determination of mercury in some pharmaceutical preparations.** J. Weyers (Medical Academy, Cracow, Poland). *Diss. Pharm.*, 1960, **12** (1), 29–34.—This method is based on the colorimetric determination of a pyridine soln. of mercury reineckate. For mersalyl a soln. is treated with conc. HCl, then heated, and a saturated soln. of Reinecke salt is added dropwise. The ppt. is washed with hot water and dissolved in pyridine. The extinction of this soln. at 530 mμ is measured against a soln. prepared by carrying a soln. of mercuric chloride through the same procedure. The results agree with those obtained by the B.P. 1948 method to within ±1%. B. K.

5008. **Microchemical identification of chlorothiazide and dihydrochlorothiazide.** E. de Zoeten (Rijks Inst. Pharmacotherap. Onderz., Leiden, Netherlands). *Pharm. Weekbl.*, 1960, **95** (6), 174–176.—Chlorothiazide and dihydrochlorothiazide can be identified by microchemical reactions with the following reagents—(*i*) Lüdy-Tenger's reagent (*Pharm. Acta Helv.*, 1944, **19**, 393) ($FeCl_3$, HCl

and KI), (*ii*) ammoniacal silver soln. and (*iii*) ammoniacal Cu acetate soln. The crystal forms of the pptd. compounds can be used for identification; 8 drawings are given. M. J. MAURICE

5009. **Polarographic estimation of Amphenone B [3:3-di-(*p*-aminophenyl)butan-2-one] and Su 4885 [2-nicotinoyl-2-(3-pyridyl)propane].** L. Stárka and I. Buben (Res. Inst. of Endocrin., Prague). *J. Pharm. Pharmacol.*, 1960, **12** (3), 175–178.—The heights of the cathodic diffusion waves of Amphenone B and Su 4885 at the dropping mercury electrode in aq. soln. are proportional to concn. The $E_{\frac{1}{2}}$ values *vs.* the S.C.E. are −1·40 and −1·22 V, respectively. A. R. ROGERS

See also Abstracts—**4686**, Hg in pharmaceutical preparations. **4854**, Micro-determination of phenylmercury compounds. **4859**, Separation of isomeric menthols. **4874**, Free menthol in peppermint oil. **4875**, Coulometric micro-determination of thymol. **4882**, Determination of starch. **4910**, Amperometric determination of penicillin. **4911**, Identification of sedatives, hypnotics and tranquillisers. **4912**, Determination of chlorpropamide. **4913**, Determination of acetazolamide. **4914**, Determination of, 4-allyl-NN-diethyl-2-methoxyacetamide. **4927**, Spray reagent for deoxy sugars. **4938**, Determination of catecholamines. **5080** Determination of lupin alkaloids.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

5010. **Flame-photometric determination of sodium in dietetic products.** H. Suter and H. Hadorn (Lab. VSK, Basel, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1960, **51** (2), 107–117.—The Beckman B spectrometer with flame attachment was used in these investigations, and, because K is usually present in larger amounts than Na, it was necessary to prepare standard curves for various concn. of K. Samples of coffee extracts were prepared by dry- and wet-ashing. Results are tabulated. It was found with dry-ashing that loss due to local overheating could not be avoided; wet-ashing is therefore recommended, although contamination from reagents is possible and a blank must be carried out. *Procedure*—The sample (0·5 to 1 g, according to the H_2O content) is digested in a 50-ml Kjeldahl flask with 1 to 2 ml of conc. H_2SO_4 with subsequent addition of 1 to 2-ml portions of HNO_3. When the soln. is slightly yellow or colourless it is cooled and made up to volume, and an aliquot is examined flame-photometrically. The standard curve (at 589 mμ) is linear for concn. of Na <3 mg per litre. The most favourable concn. of K depends on the sensitivity of the apparatus used; in the investigation described it was between 4 and 16 mg per litre. Results for the determination of Na and K in NaCl-free crisp-bread, beans, sauces, sandwich spread, mustard and dietetic salts are given.

I. DICKINSON

5011. **Colorimetric determination of phosphate in sugar products.** J. J. Cincotta (Applied Sugar Lab., American Molasses Co., Brooklyn 31, New York). *J. Agric. Food Chem.*, 1960, **8** (2), 145–147.—Total P is determined in sugar products by digestion with HNO_3 and H_2SO_4 to destroy organic material and hydrolyse sugar phosphates, and colorimetric measurement of P at 420 mμ as the yellow compound formed on addition of ammonium vanadate and ammonium molybdate. Inorganic P is determined by the same procedure, but omitting the acid digestion. Silicate does not interfere at the prescribed acid concn. of 1·5 *N*, though it does at a concn of 0·5 *N*, found to be optimum by Kitson and Mellon for other applications of the method (*cf. Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 379).

M. D. ANDERSON

5012. **Determination of small amounts of arsenic in potatoes. Extraction and reduction of molybdoarsenic acid.** D. J. Lisk (New York State Coll. of Agric., Cornell Univ., Ithaca, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (2), 121–123.—In Wadelin and Mellin's modification (*Analyst*, 1952, **78**, 708) of Akkseev's procedure (*Zavod. Lab.*, 1945, **11**, 122) the As is measured as molybdoarsenic acid (**I**), which is extracted from the sample by *n*-butanol, after removal of interfering P as molybdophosphoric acid by extraction with *n*-butanol - $CHCl_3$. The method is not quite sensitive enough for determining traces of As in biological materials. It is adapted for such use by acidifying the butanol extract with H_2SO_4 - ethanol, and reducing **I** to molybdenum blue with $SnCl_2$ in ethanol. Interference by Si occurs if the content of Si is above 8 p.p.m.; this can be lessened by using *n*-butanol - ethyl acetate for extracting **I**. When the method was used to determine traces of As (1 to 8 p.p.m.) added to potatoes the mean recovery was 94%.

M. D. ANDERSON

5013. **Continuous electrophoresis of wheat gluten.** H. Zentner (Bread Res. Inst. of Australia, Sydney). *Chem. & Ind.*, 1960, (12), 317–318.—The separation of seven protein fractions from wheat gluten by electrophoresis on a curtain of Whatman 31 ET paper, with 0·01 *M* lactic acid as electrolyte, is briefly described. The main fraction (54%) was a lipoprotein, which stained with Oil Red O (C.I. Solvent Red 27) and contained unidentified carbohydrate material. E. C. APLING

5014. **Determination of water-dispersible protein in soya bean oil meals and flours.** T. M. Paulsen, K. E. Holt and R. E. Anderson (Archer-Daniels-Midland Co., Minneapolis, Minn.). *J. Amer. Oil Chem. Soc.*, 1960, **37** (4), 165–171.—The development of an improved Waring Blendor method is described and results are compared with those of existing procedures. The effects of blending speed, temp., time, pH and design of blade were studied. Using a Hamilton Beach Drinkmaster with Waring Blendor blades and cups, samples (20 g) were blended at 8500 r.p.m. for 10 min. at 25 ±1°, followed by centrifuging of an aliquot at 2700 r.p.m. for 10 min. and nitrogen determination. Results showed a high degree of accuracy and there was excellent correlation between the processing control results and the end-product uses.

P. M. KINGSTON

5015. **Indirect polarographic determination of nitrates in biological material.** E. Davídkova and J. Davídek (Central. Res. Inst. of the Food Industry, Prague). *Z. LebensmittUntersuch.*, 1960, **111** (6), 477–483.—The method is based on the colorimetric determination of nitrates with 2:4-xylenol in strongly acid medium. The 6-nitro-2:4-xylenol produced is steam-distilled and determined polarographically in alkaline medium. Nitrate soln. (5 ml)

and 20 ml of 85% H_2SO_4 are pipetted into a 250-ml flask, the mixture is cooled to room temperature, and 1 ml of 2% 2:4-xylenol soln. in acetone is added. Nitration is complete in 20 min., then 100 ml of water and some pumice are added, and the mixture is steam-distilled into 5 ml of 4 *N* NaOH in a 50-ml flask. When about 45 ml has distilled, 0·5 ml of 0·5% gelatin soln. is added, the soln. is made up to vol. and the polarogram is recorded. Nitrite, if present in the initial soln., can be removed by conversion into the methyl ester and distillation; halides by means of 85% H_2SO_4 saturated with silver sulphate. The method, depending on a 6-electron reduction, is very sensitive, and results are linear over a wide range. Results of determinations in sausage, meat, preserving salt and brines show good agreement with those of the colorimetric method. C. L. HINTON

5016. **Rapid determination of egg content in "pasta all'uovo."** V. Chioffi (Lab. Chim. Provinciale, Rovigo, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (1), 60–66.—The method depends on the colorimetric determination of cholesterol in an acetone extract of the pasta by the method of Zlatkis (*J. Lab. Clin. Med.*, 1953, **41**, 486). *Procedure*—Mix the sample (1 g) with pumice (1 g) and extract under reflux with acetone (20 ml), with gentle shaking, for 20 min. Allow to settle and filter or centrifuge. Evaporate an aliquot of the filtrate (1 ml) to dryness, cool, add a 0·1% soln. of $FeCl_3.6H_2O$ in glacial acetic acid (5 ml) and conc. sulphuric acid (3 ml). Shake for 25 to 30 min., centrifuge to remove air bubbles and measure the extinction at 560 mμ in a 1-cm cell. The extinctions calculated on the dry matter were found to vary from 0·125 for zero egg content to 0·495 for 6 eggs per kg. E. C. APLING

5017. **Accuracy of the Gerber test for the determination of fat in milk.** J. H. Labuschagne and K. F. Vogt (Div. Animal Husbandry and Dairying, Pretoria). *S. Afr. J. Agric. Sci.*, 1960, **3** (1), 83–89.—A statistical analysis of results obtained on 413 milk samples shows that over the normal range of fat contents the Gerber method (11-ml pipette) gives higher values than the Röse - Gottlieb gravimetric method, the relationship between the values being $G = 1{\cdot}041 \times R.G. - 0{\cdot}058$. In order to obtain agreement at a fat content of 3·50% (average for South African milk) the delivery of the milk pipette must be reduced to 10·74 ml. When such a pipette (or the Netherlands 10·77-ml pipette) is used, the agreement between the two methods is satisfactory over a wide range of fat contents. The density and s.n.f. content of the milk have a statistically significant effect on the differences between the results obtained by the two methods, but for practical purposes this is negligible. S. M. MARSH

5018. **Standardisation of butyrometers for milk. The present position.** J. Pien. *Ann. Falsif.*, 1960, **53**, 119–131.—The historical development of butyrometric methods is related to the present-day standardisation of the Gerber method. It is shown that, with the classical 11-ml pipette, Gerber results are somewhat high in terms of grams of fat per kg of milk, but are almost exact in terms of grams per litre. E. C. APLING

5019 **Complexometric titration of calcium and magnesium in the presence of phosphate in milk and blood plasma.** T. H. Kamal (Dept. of Dairy Husbandry, Univ. Missouri, Columbia, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (2), 156–158.—Calcium and Mg in biological materials, *e.g.*, in milk and blood plasma, are determined by adding an excess of EDTA (disodium salt) to a neutral system, and back-titrating the excess with standard soln. of Ca and Mg, with calcein as indicator for Ca, and Eriochrome black T for Mg. This method avoids the necessity of removing P and protein, and is rapid and sensitive. M. D. ANDERSON

5020. **Rapid determination of minerals and ions in milk. II. Determination of chloride.** V. R. Wenner (Nestlé Products, Vevey, Switzerland). *J. Dairy Sci.*, 1960, **43** (1), 22–27.—A description is given of a volumetric method requiring titration with $Hg(NO_3)_2$ in 1% HNO_3 and is suitable for milk and many milk products. For Cl^- concn. below 10 mg per 100 ml, the method is not satisfactory. A rapid accurate potentiometric method is based on the potential between a silver - silver chloride and a palladium - mercury - calomel reference electrode immersed in the sample. The Cl^- concn. may be read directly from a calibration graph, with an accuracy of +5 to +2% according to the sensitivity of the potentiometer. In the presence of free amino acids or other substances capable of dissolving AgCl, preliminary treatment with aq. $CuSO_4$ soln. is required. W. H. C. SHAW

5021. **The use of turbidimetric methods for testing homogenised milk.** J. D. S. Goulden (Nat. Inst. Res. Dairying, Shinfield, Reading, England). *J. Dairy Res.*, 1960, **27** (1), 67–75.—A study is made of the factors affecting spectroturbidimetric methods for testing the degree of homogenisation of milk. The effects of alkali addition, the optical system, dilution, fat content, homogenisation pressure, heating and sterilisation and theoretical aspects are considered. It is concluded that, provided care is exercised in the design of the instrument, the turbidity index at a given wavelength measured on a simple filter turbidimeter provides a useful practical measure of the degree of homogenisation. W. H. C. SHAW

5022. **Reviews on the progress of dairy science. The chemistry of butter and butter fat.** E. G. Pont (C.S.I.R.O., Melbourne, Victoria, Australia). *J. Dairy Res.*, 1960, **27** (1), 121–150.—This review includes sections on the analysis of butter and butter fat and on the detection of adulteration. W. H. C. SHAW

5023. **Colorimetric determination of the cupric salt of pectic acid.** M. Kaláb (Gastroenterol. Lab., Med. Fac., Palacký Univ., Olomouc, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 960–963 (in German).—The colour change of the complex of Cu^{II} with aq. NH_3 after the reaction with EDTA (disodium salt) (**I**) was used for a rapid colorimetric method. *Procedure*—Dissolve the pectin sample in H_2O (200 ml), hydrolyse, neutralise with acetic acid to phenol red and dilute with H_2O to 250 ml. To an aliquot (5 to 20 ml) add H_2O (50 ml) and $CuSO_4.5H_2O$ soln. (1%) (15 ml). Filter off the ppt., wash it with H_2O, dissolve it on the filter in *N* aq. NH_3, transfer the soln. into a test-tube containing 0·1 g of **I**, mix (the colour turns bright green) and measure the extinction at 619 mμ. Carry out a blank test. The accuracy is within ±6·5%. Aluminium and Fe interfere. The pptd. Cu salt of

pectic acid can also be filtered off, dried for 12 hr. at 105°, and weighed, and the Cu content determined in the residue. J. ZÝKA

5024. **The amino acids of spirit vinegar. II. Quantitative determination of amino acids; differentiation of fermentation and synthetic vinegar.** K. G. Bergner and H. R. Petri (Chem. Landesuntersuchungsanst., Stuttgart). *Z. LebensmittUntersuch.*, 1960, **111** (6), 494–504.—The trace amounts of total amino acids isolated by the ion-exchange method (*cf. Ibid.*, 1960, **III**, 319) were determined by formation of their copper complexes by treatment with copper phosphate at pH 7·4, the copper being then determined colorimetrically with diethyldithiocarbamate. Amounts found in different spirit vinegars were between 3·1 and 11·4 mg per litre, depending on the mode of preparation of the vinegars and increasing with storage in the presence of bacteria. Vinegars of different bacterial origin produced under similar conditions should show no significant differences in amino-acid composition. A method is described for distinguishing fermentation vinegar from synthetic. The sample (200 ml or less) is evaporated to dryness in platinum and the residue is extracted with 10 ml of acetone containing 0·5% of conc. HCl. After evaporation of the acetone the residue is dissolved in 2 drops of H_2O and chromatographed on a filter disc (S. & S. 2043b Mgl) lying on a 2-cm layer of cellulose powder saturated with *n*-butanol - glacial acetic acid - water (4:1:5). Total amino acids are developed on one segment with ninhydrin, and proline on another with isatin. In tests on vinegars of known origin the amino-acid spots were well defined with the fermentation vinegars and absent with the synthetic. Caramel and an acetic acid extract of cork did not interfere. C. L. HINTON

5025. **Complexometric determination of propyl gallate.** Z. Malkus and J. Horáček (Inst. Hygiene, Prague). *Průmysl Potravin*, 1960, **11** (1), 43–45.—The method is based on the pptn. of gallate with an excess of bismuth nitrate (1 mole of propyl gallate reacts with 1 mole of Bi^{3+}) and the complexometric determination of the excess of Bi, with catechol violet or xylenol orange as indicator. *Procedure*—Dissolve the sample (0·1 g) in H_2O, heat and precipitate with 0·05 *M* $Bi(NO_3)_3$ in acetic acid. Mix, cool and filter, then wash the ppt. with 1% acetic acid and a few ml of H_2O. To the filtrate add 3 to 5 drops of conc. HNO_3, and catechol violet soln. (0·1%) (5 drops) as indicator and titrate with 0·05 *M* EDTA (disodium salt) till the colour becomes yellow. Small amounts of some preservatives, *e.g.*, sorbic acid or Na benzoate, do not interfere. J. ZÝKA

5026. **Detection of mineral oil in roasted coffee.** B. Doro and G. Gabucci (Lab. Chim. Provinciale, Trieste, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (1), 52–59.—The method of Marotta and Alessandrini (*Ann. Chim. Appl.*, 1929, **18**, 37) and the Swiss official method (Manuel Suisse des Denrées Alimentaire, 4th ed., Berne, 1939, p. 238) are compared; the Swiss method is preferred. Chromatography on alumina for the detection of mineral oil according to the method of Cotta-Ramusino (*R.C. Ist. Sup. Sanit.*, 1959, **21**, 313) is advised for all samples of roast coffee having unsaponifiable matter in excess of 0·1%. A brief description and tabulated analytical figures are given for a number of commercial types of coffee. E. C. APLING

5027. **Tests with the Rebelein method for distinguishing naturally pure and sweetened wines.** K. Hennig and A. Lay (Inst. f. Biochem. u. Weinchem., Geisenheim, Germany). *Z. Lebensmitt-Untersuch.*, 1960, **111** (6), 505-512.—The method of Rebelein (*Anal. Abstr.*, 1958, **5**, 700) for distinguishing between naturally pure and sweetened wines, based on glycerol and butane-2:3-diol contents, was applied to 60 wines of 1954 to 1958 and a few earlier ones, produced under close control throughout. Of the results, tabulated individually, 45% were unsatisfactory. It is concluded that the method cannot be used for legal purposes. C. L. HINTON

5028. **Analysis of fats and oils by gas - liquid chromatography and by ultra-violet spectrophotometry.** S. F. Herb, P. Magidman and R. W. Riemenschneider (Eastern Regional Res. Lab., Philadelphia, Penn.). *J. Amer. Oil Chem. Soc.*, 1960, **37** (3), 127–129.—Experiments were carried out to obtain more information on the quant. aspects of gas - liquid chromatography as a practical analytical technique for determining the fatty-acid composition of natural fats and oils. Analyses of known mixtures of pure fatty-acid esters and of a series of fats and oils were compared with known values or with analyses by an alkali-isomerisation u.v. spectrophotometric method. The type of equipment (thermal conductivity detector), column packing and operation are described. It was found that the percentage of fatty acid distribution determined by gas - liquid chromatography agreed well with known percentages in model mixtures and with analyses by the spectrophotometric method for fats and oils, but the determination of traces of arachidonic and pentenoic acids in lard by this method was not successful. I. DICKINSON

5029. **Rapid determination of monoglycerides in the process of transesterification of fats by glycerol.** E. Mareš (Res. Inst. Fat Industry, Ústí Nad Labem, Czechoslovakia). *Průmysl Potravin*, 1959, **10** (12), 650–652.—A new rapid method for the determination of monoglycerides in the fat phase of the reaction mixture of the transesterification of solidified vegetable fats with glycerol at 170° to 180° in the presence of 0·25% KOH as catalyst is based on the determination of the difference between the dielectric constants of the original fat and of the fat phase of the reaction mixture. The time required is 5 min. and the average error is $\pm 1\%$ of monoglycerides. The apparatus used is based on the resonance principle at a frequency of 1 Mc per sec. J. ZÝKA

5030. **Possibility of obtaining a judgment of the genuineness of edible oils by fractionation of the glycerides.** F. Mangio (Lab. Chim. Provinciale, Livorno, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (1), 12–44.—The fractionation of the glycerides of oils at constant temperature by precipitation from acetone soln. by known additions of water gives glyceride fractions the iodine values of which are reproducible. A "fractionation index" is defined which is constant for a given oil. Results obtained with virgin and rectified olive oils, arachis, tea-seed, soya bean, cottonseed, rape and lard oils and some binary and ternary mixtures are tabulated and the use of the fractionation index in the examination of oils is discussed. E. C. APLING

5031. **Estimation of unsaturation of fats and oils using hypochlorous acid.** R. Basu Roy Choudhury

(Iowa State Univ., Ames, U.S.A.). *J. Amer. Oil Chem. Soc.*, 1960, **37** (4), 198–199.—Acidified commercial bleaching solution (Chlorox) has been used as a simple reagent for determining conjugated and non-conjugated unsaturation. The oil or fat (0·1 to 0·2 g) is treated with 10 ml of glacial acetic acid followed by 25 ml of 0·1 *N* bleach solution. After 10 min., the mixture is treated with 15% KI soln. and the iodine is titrated in the usual way. Results for 9 oils showed good agreement with those by Wijs, pure HOCl and other methods.

P. M. KINGSTON

5032. **Determination of free fatty acids in fat.** I. Hornstein, J. A. Alford, L. E. Elliott and P. F. Crowe (Meat Lab., Agric. Res. Service, U.S. Dept. of Agric., Beltsville, Md.). *Anal. Chem.*, 1960, **32** (4), 540–542.—Naturally occurring free fatty acids in cooked and cured meats are adsorbed on Amberlite IRA-400, and are converted into methyl esters directly on the resin with anhydrous methanol - HCl (5 to 10% of acid). The esters are analysed by gas chromatography on a poly(vinyl acetate) column, quantitative determination being made with *n*-heptadecanoic acid as internal standard.

H. F. W. KIRKPATRICK

5033. **Variation with refining of the characteristics of [olive] oil. II. Iodine value of the unsaponifiable matter.** G. B. Martinenghi (Studio di Ricerche per Olii, Milan). *Olii Min.*, 1960, **37** (3), 88–92.—The iodine val. of the unsaponifiable matter is not a reliable index for detecting the adulteration of olive oils, particularly refined and esterified oils. The value is affected by the treatment given to the oil, and vigorous deodorisation will raise the iodine val. of the unsaponifiable matter of arachis oil or tallow to that of olive oil.

L. A. O'NEILL

5034. **Spectrofluorimetric studies on olive oil.** F. Provvedi (Lab. Chim. Provinciale, Bergamo, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (1), 3–7.—The results of the examination of pure and rectified olive oils by means of Farrand spectrofluorimeters are reported. Pure expressed oils show a weak fluorescence excited by light of wavelength 315 mμ, and none at 360 mμ. Rectified oils are distinguished by showing strong fluorescence, with a maximum in response to light of wavelength 360 to 365 mμ.

E. C. APLING

5035. **Paper chromatography in the field of fats. XL. Analysis of mixtures of fatty acids.** H. P. Kaufmann and Z. Makus (Dtsch. Inst. für Fettforschung, Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1960, **62** (3), 153–160.—The separation of mixtures of odd- and even-numbered fatty acids from C_7 to C_{28} is achieved on paper impregnated with undecane, with aq. acetic acid as mobile phase. The existence of "critical pairs" (two fatty acids with identical R_F values) has been investigated.

A. R. ROGERS

5036. **Quantitative paper chromatography of higher fatty acids in the form of methyl esters ($R{\cdot}COO{\cdot}^{14}CH_3$).** B. P. Smirnov, R. A. Popova and R. A. Niskanen (Inst. of Biol., Acad. USSR, Petrozavodsk). *Biokhimiya*, 1960, **25** (2), 368–375.—Higher fatty acids are methylated by means of diazomethane ($^{14}CH_2N_2$). The methyl esters are separated by paper chromatography and determined quantitatively by autoradigoraphy of the chromatograms and planimetric treatment of the photometric curves. The paper is made hydrophobic with soft paraffin and the solvents used are acetic acid - acetone (3:1), methanol - acetone (2:1 and 3:1) and ethanol - acetone (2:1). Data are presented on the content of individual higher fatty acids in castor and arachis oil.

A. BURWOOD-SMITH

5037. **Colorimetric reactions of unsaturated fatty acids with metal salts.** D. N. Rhodes (Low Temp. Res. Sta., Cambridge, England). *J. Appl. Chem.*, 1960, **10** (3), 122–124.—Coloured products having characteristic absorption spectra are formed when pure esters and glycerides of oleic, linoleic and linolenic acids are treated with $FeCl_3$ or mercuric acetate (**I**) in the presence of glacial acetic acid and conc. H_2SO_4. Under controlled conditions, the reaction provides a method for the spectrophotometric determination of these acids in natural fats and oils. To obviate the low solubility of linoleic-poor fats, *e.g.*, olive oil or lard, in the reagent mixture, partial transmethylation of the sample is sometimes necessary. *Procedure*—To glacial acetic acid (4 ml) containing $FeCl_3$ (0·0025%, w/v) or **I** soln. (0·05%, w/v) add conc. H_2SO_4 (3 ml), shake the mixture vigorously (in a stoppered test-tube) and keep it for ≃5 min. in a water bath at 60°. Then add the sample (dissolved in 1 ml of acetic acid) and, after shaking, keep the mixture at 60° for 20 min. Cool the viscous soln., pour it into a 1-cm cell, remove the bubbles by evacuation and measure the extinction at 478 mμ (when $FeCl_3$ is used) or 405 mμ (when **I** is used). Beer's law is followed; **I** is more sensitive than is $FeCl_3$ with oleic and linoleic esters, but the colour with linolenic esters is weaker. The sample should not contain polyenes higher than triene.

W. J. BAKER

See also Abstracts—**4825**, Determination of volatile flavouring constituents of vegetables. **4948**, Determination of glutamic acid.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

5038. **Efficiency of absorbers in industrial hygiene air analysis.** J. C. Gage (I.C.I. Ltd., Industrial Hygiene Res. Lab., The Frythe, Welwyn, Herts., England). *Analyst*, 1960, **85**, 196–203.—The principles involved in the use of liquid absorbers for air sampling in the analytical control of atmospheric contamination are reviewed. Test atmospheres artifically impregnated with ethylene oxide or chlorobenzene were used to study the effects of vol. of air sample, rate of sampling and design of the absorber (3 types) on the efficiency of absorption. Ethylene oxide was absorbed in water at 25° and its concn. was determined spectrophotometrically (*Analyst*, 1957, **82**, 587). Chlorobenzene was absorbed in a soln. of paraformaldehyde in conc. H_2SO_4, and the extinction of the soln. was measured at 485 mμ. The results are tabulated and discussed.

A. O. JONES

5039. **Photometric determination of acrylic and methacrylic acid ester monomers in the atmosphere.** V. Šedivec (Inst. Hyg. and Ind. Diseases, Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 897–905 (in German).—The monomers are passed into cooled *iso*propyl alcohol, converted into the corresponding hydroxamic acids and

determined photometrically after reaction with Fe^{3+}. *Procedure*—Cool a flask containing *iso*propyl alcohol (10 ml) with a mixture of ice and salt (3:1). Through the cooled liquid pass 10 to 25 litres of the air (0·2 to 0·4 litre per min.). Transfer the contents into a 25-ml flask and wash with H_2O (5 ml). To the combined liquids add at 20° a soln. of hydroxyammonium chloride (17·3%) (1·5 ml), mix thoroughly and set aside for 10 to 20 min. (for acrylates) or for 30 to 40 min. (for methacrylates), with occasional shaking. Add $FeCl_3$ soln. (27 g of $FeCl_3.6H_2O$ and 300 ml of 2·5 *N* HCl in 500 ml of H_2O) (5 ml) and shake till the $Fe(OH)_3$ dissolves. Dilute with H_2O to 25 ml and measure the red colour at 530 mμ (green filter) against a blank. Compare with a calibration curve. For 0·2 to 25 mg of methyl acrylate the accuracy is ±3% (relative). Volatile esters, anhydrides or chlorides of other organic acids which react in a similar way and large amounts of aldehydes and ketones interfere, but not alcohols or aliphatic and aromatic hydrocarbons. Good results were obtained with artificial samples of methyl, ethyl and butyl acrylates and methyl methacrylate.

J. ZÝKA

5040. **Qualitative detection of phosgene [in air].** Yu. N. Forostyan and G. V. Lazur'evskiĭ. USSR Pat. 122,634 (18.9.59).—Filter-paper soaked in anabasine or in a mixture with related alkaloids turns a purple to intense red colour on contact with an atmosphere containing phosgene; the limiting concn. is 0·0003 mg per litre. No reaction is obtained with other halogen compounds.

C. D. KOPKIN

5041. **Improved method for the determination of nitrates in water by means of back-titration of an excess of indigocarmine with permanganate.** D. Ceauşescu (Inst. Hyg., Timişoara). *Rev. Chim., Bucharest*, 1960, **11** (3), 173–175.—The method is an improvement on that previously proposed (*cf. Anal. Abstr.*, 1959, **6**, 3794). *Procedure*—The sample (5 ml) is treated with 0·3 ml of 2 *M* NaOH and 0·5 ml of 0·004 *M* $KMnO_4$. The mixture is heated for 5 min. in boiling water, and 0·6 ml of dil. H_2SO_4 (1:3) is added, followed by 0·02 *M* oxalic acid until the soln. is decolorised. Water is added to 8 ml and the mixture is treated with 0·2 ml of NaCl soln. (20%), 5 ml of indigocarmine soln. (0·001 *M*) [indigocarmine (0·4662 g) and 20 ml of dil. H_2SO_4 (1:5) in 1 ltrie] and 13 ml of conc. H_2SO_4. After heating for 2 to 3 min. in boiling water, the tube is washed out with 25 ml of water and the soln. is titrated slowly with 0·0004 *M* $KMnO_4$ until the colour changes sharply from blue through green to yellow. A standard curve is prepared by treating various amounts of KNO_3 as above except that, after addition of the alkali and $KMnO_4$, the samples are not boiled for 5 min., but heated to between 80° and 100°. The method can be used for concn. up to 60 mg of NO_3^- per litre; the sensitivity is within 0·05 to 0·1 ml of 0·0004 *M* $KMnO_4$.

H. SHER

5042. **Determination of radioactive strontium in reservoir waters.** L. K. Ponomareva and V. L. Zolotavin. *Radiokhimiya*, 1959, **1**, 208–211.—Strontium is first concentrated by a carbonate pptn. from 5 litres of water; Ca is separated by pptn. with fuming HNO_3. The total ^{90}Sr plus ^{89}Sr content is thus determined in 2 hr. with a max. error of ±10%. Strontium-90 alone is determined, with a max. error of ±10%, by counting the ^{90}Y daughter 24 hr. later. As little as 5×10^{-11} C of ^{90}Sr per litre can be determined by these methods, an order of magnitude lower than the maximum permissible concn. in water.

NUCL. SCI. ABSTR.

5043. **Determination of trace quantities of silver in trade effluents. Report to the Analytical Methods Committee of the Society for Analytical Chemistry of work carried out at Oxford.** T. B. Pierce. *Analyst*, 1960, **85**, 166–177.—The silver is extracted from the sample soln., acidified with H_2SO_4, with a soln. of dithizone in CCl_4. The aq. layer is discarded from the centrifuged mixture and the CCl_4 layer is extracted with aq. NH_4SCN soln. The aq. extract is evaporated to dryness with H_2SO_4, the residue is dissolved in HNO_3 and the soln. is digested with hydroxyammonium sulphate and urea. The cooled liquid is rinsed into a micro-separator (described) with 0·5 *N* H_2SO_4 and is extracted with a dil. soln. of dithizone in CCl_4. The colour of the extract is compared visually with standards, or is measured either in a Spekker absorptiometer with Ilford orange filter No. 607 or in a spectrophotometer at 620 mμ, and referred to a calibration graph.

A. O. JONES

See also Abstracts—**4677**, Radio-barium in sea water. **4719**, Zr in industrial wastes. **4817**, Chromatographic separation of H, N and CH_4 in natural water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

5044. **Direct-reading spectrochemical method for the analysis of plant material.** W. J. Pienaar (W. Province Fruit Res. Sta., Stellenbosch). *S. Afr. J. Agric. Sci.*, 1960, **3** (1), 57–68.—Magnesium, Mn and Cu are determined by a d.c. arc procedure. Plant ash is mixed (1:10) with a buffer mixture made by adding 12 ml of 1% Sn soln. (internal standard) to 15 g of graphite and, after drying at 110°, adding the mixture to 10 g of Li_2CO_3. The test mixture is filled into graphite electrodes and an arc applied directly. The line intensities are measured photometrically. Full details of the apparatus, with circuit diagram, are given. The reproducibility and accuracy of the method are comparable with those of other routine analytical procedures for all three elements.

S. M. MARSH

5045. **Quantitative paper chromatography of inorganic ions in soils and plants.** C. B. Coulson, R. I. Davies and C. Luna (Dept. of Agric. Chem., School of Agric., Univ. Coll. of N. Wales, Bangor, Gt. Britain). *Analyst*, 1960, **85**, 203–207.—From an oxidised extract of the soil under appropriate conditions Cu, Co and Zn are extracted with a soln. of dithizone in $CHCl_3$, and, after the addition of dimethylglyoxime to the aq. liquid, the nickel complex is extracted with $CHCl_3$. The solvent is removed from the combined extracts, the residue is evaporated repeatedly with HCl and finally dissolved in HCl, the vol. of the soln. being reduced to 0·15 ml. From an aliquot of this the metals are separated by ascending paper chromatography with an acetone - ethyl acetate - 6 *N* HCl mixture as solvent. Ethanolic dithio-oxamide soln. is used to identify Cu, Ni and Co, and 1-nitroso-2-naphthol soln. to identify low concn. of Co. To determine Cu, Co and Ni, a double-beam reflectance densitometer (Ayers, *Mikrochim. Acta*, 1956, 1333) is used. Zinc is determined colorimetrically. With slight modification the method is applied to plant material oxidised with H_2SO_4, HNO_3 and $HClO_4$.

A. O. JONES

5046. **Application of thermogravimetry to the analysis of carbonates occurring in soils. I. Analysis of pure carbonates and naturally occurring limestones.** J. R. Wright, I. Hoffman and M. Schnitzer (Res. Branch, Canada Dept. of Agric., Ottawa). *J. Sci. Food Agric.*, 1960, **11** (3), 163–167.—Thermogravimetry in an atmosphere of CO_2 permits the accurate determination of total carbonates, and partitioning into calcite and dolomite, in one operation. The method is generally more sensitive than chemical analysis, and the results are confirmed by X-ray measurements. The procedure is especially useful in the case of natural limestone samples, since the assumption of a Ca to Mg ratio of 1:1 for dolomite may lead to serious errors in the chemical analysis.

II. Analysis of carbonates in soil. I. Hoffman, M. Schnitzer and J. R. Wright. *Ibid.*, 1960, **11** (3), 167–172.—The values for total carbonates in soils given by thermogravimetric analysis were in good agreement with chemical determinations. For most soils where partitioning was possible, the results for dolomite were higher, and those for calcite lower, than values obtained chemically. This difficulty was traced to an interaction between Na and/or K and Si with calcite; it was shown experimentally that Na, K and Ba, in the presence of quartz, have a marked effect in lowering the temp. at which the decomposition of calcite commences.

D. C. ARMSWORTH

5047. **Photometric determination of boron [in plants] by the carmine method.** P. I. Nikishkina. *Pochvovedenie*, 1959, (9), 107–109; *Ref. Zhur., Khim.*, 1960, (4), Abstr. No. 13,106.—To determine B in plants, moisten 0·5 to 1 g of dry plant material in a platinum crucible with 1% KOH soln., evaporate to dryness and ash at 500° to 550°. Dissolve the residue by heating with 5 to 10 ml of 0·5 *N* H_2SO_4 and filter. To 1 ml of filtrate add 19 ml of a 0·005% soln. of carmine in H_2SO_4 (sp. gr. 1·84) and mix. After 2 hr. measure the extinction in a photocolorimeter, using as filter a 0·005% carmine soln. with water as comparison. To determine water-soluble B in soil, add 100 or 200 ml of water to 50 or 100 g of the air-dry sample and boil under reflux for 5 min., cool and filter. Evaporate an aliquot to dryness in a quartz dish, moisten the residue with 0·5 *N* H_2SO_4 containing 2 g of hydrazine sulphate per litre and ignite till no more SO_3 fumes are evolved. Dissolve the residue in 5 or 10 ml of 0·5 *N* H_2SO_4, filter and determine B in 1 ml of filtrate. The sensitivity of the method is 0·5 to 10 μg of B per ml.

C. D. KOPKIN

5048. **Determination of the cement or lime content of stabilised ferruginous soils.** P. T. Sherwood (Road Res. Lab., Harmondsworth, Middx., England). *J. Appl. Chem.*, 1960, **10** (3), 121–122.—Because of co-pptn. of an approx. constant amount of Ca with the sesquioxides, the direct EDTA method described previously (*cf. Anal. Abstr.*, 1958, **5**, 2659) is liable to error when applied to lateritic tropical soils stabilised with cement or lime. The error is minimised if the soil itself contains Ca; but if the soil contains little or no Ca and a high content of Fe or Al, or both, and is stabilised with a low proportion (<10%) of lime or cement, a double pptn. of the mixed oxides is necessary.

W. J. BAKER

5049. **Extraction and determination of ethylene dibromide in soils.** J. J. Jurinak, A. L. Brown and P. E. Martin (Dept. of Soils and Plant Nutrition, Univ. California, Davis, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (2), 113–115.—Dibromoethane (**I**) in soils is determined by vacuum distillation of a sample mixed with glycerol; the distillate is collected in NaOH and H_2O_2, and **I** is converted into inorganic bromide by catalytic oxidation with an electrically heated platinum wire; the Br^- are titrated with $AgNO_3$. Recovery over the range 164 to 0·4 mg of **I** per 100 g of soil fell from ≃98 to ≃75%, and was somewhat decreased when the soil was moist instead of air-dried, when the soil had a high content of organic matter, and when the glycerol was omitted.

M. D. ANDERSON

5050. **Determination of digestible carbohydrates in poultry foods.** W. Bolton (Agric. Res. Council, Poultry Res. Centre, Edinburgh, Gt. Britain). *Analyst*, 1960, **85**, 189–192.—The sample (1 g) is boiled with water until the starches are gelatinised. The cooled liquid, acidified with acetic acid, is incubated with taka-diastase at 37° overnight. It is then filtered hot and the filtrate with washings is clarified with $ZnSO_4$ and $K_4Fe(CN)_6$, made ≃1·5 *N* with respect to H_2SO_4 and heated in steam for 2 hr. The cooled liquid is neutralised and the sugar content is determined by titration with Fehling's soln. (glucose × 0·91 = available carbohydrate). When the results were compared statistically with those of digestibility trials it was found that available carbohydrate +4·9 is a reasonable measure of the digestible carbohydrate in foods for adult and growing poultry. For young chicks 4·9 should be replaced by 2·5. The compositions of some compounded diets and foods are given.

A. O. JONES

5051. **Analysis of phenoxyacetic acid compounds by an indirect method.** S. Petrașcu, E. Grou and G. Ballif (Inst. Cercet. Agron., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **7** (4), 549–568.—The herbicide 2:4-dichlorophenoxyacetic acid contains small quantities of the *o*- and *p*-chloro acids, and 2:4:5- and 2:4:6-trichloro acids. From experiments with binary mixtures of pure acids, three methods for the determination of the compounds in the technical product have been developed. (*a*) Indirect analysis by titration of total carboxyl with 0·1 *N* alkali.—The mixed indicator (equal vol. of 0·2% soln. of bromocresol green and bromothymol blue) must be used to give a sharp end-point between pH 6·2 and 6·4; the result is then as accurate as a potentiometric titration. (*b*) Indirect analysis by determination of total Cl.—For the reduction of the compound the Busch method, *i.e.*, catalytic reduction in the presence of Pd with hydrazine hydrate, is recommended. For the determination of Cl^- the potentiometric method with calomel and silver electrodes is used. (*c*) Indirect method of analysis of technical mixtures by determination of total carboxyl and chlorine.

H. SHER

5052. **Chloromethylphenoxyacetic acid. Chromatographic separation of isomers and related acids.** F. Martin and M. Pallière (Lab. de Rech. Anal., Soc. des Usines Rhône-Poulenc, France). *Bull. Soc. Chim. France*, 1960, (2), 375–377.—Commercial "methylchlorophenoxyacetic acid" may contain 4-chloro-2-methylphenoxyacetic acid (**I**), 6-chloro-2-methylphenoxyacetic acid (**II**), dichloromethylphenoxyacetic acid (**III**) and 2-methylphenoxyacetic acid (**IV**). *Procedure*—A column of 20 g of acid-extracted Celite (Si-O-Cel C_{22}) is mixed with 12 ml

of phosphate buffer (pH 6·6) saturated with ether and made into a slurry with ether - *cyclo*hexane (1:1), and introduced into a column of internal diam. 10 to 11 mm. The sample (0·7 g) is dissolved and made up to 100 ml with ether - *cyclo*hexane (1:1) saturated with the buffer. The column is eluted with ≃125 ml of the same solvent at ≃45 ml per hr. and collected in 4 to 5-ml fractions, which are titrated with 0·005 *N* NaOH in the absence of CO_2, with 0·4% aq. bromothymol blue as indicator. This determines **III**. **I** is similarly eluted with ether saturated with buffer (100 ml) and titrated, and **II** with ether - *tert.*-amyl alcohol (9:1) (100 ml) saturated with buffer. **IV** is then eluted with ether - *tert.*-amyl alcohol (23:2) (100 ml) saturated with buffer. E. J. H. Birch

5053. **Analysis of 2:4:5-trichlorophenoxyacetic acid *iso*propyl ester and 2:4:5-trichlorophenoxyacetic acid butyl ester mixtures.** D. N. Thomas (Chipman Chem. Co., Portland, Ore.). *Anal. Chem.*, 1960, **32** (3), 441.—Infra-red data are given.

5054. **Detection and estimation of the biologically active constituents of pyrethrum.** H. J. Smith (The Pyrethrum Board, Nakuru, Kenya). *J. Sci. Food Agric.*, 1960, **11** (3), 172–176.—A rapid method for the routine determination of cinerin I, pyrethrin I, cinerin II and pyrethrin II in pyrethrum preparations is based on the quant. preparation and chromatographic separation of the 2:4-dinitrophenylhydrazones. *Procedure*—Pyrethrum extract (150 to 160 mg) is dissolved in 2·5 ml of ethyl ether and 6·5 ml of methanol added slowly with swirling. 2:4-Dinitrophenylhydrazine (70 mg) and methanolic HCl [1 ml of a mixture of conc. HCl (3 ml) and methanol (25 ml)] are added. The mixture is kept at room temp. for 3·5 hr. with occasional swirling and then transferred to a separating-funnel containing 50 ml of H_2O with the aid of 50 ml of isohexane (Shell). The aq. layer is separated after mixing, and re-extracted with isohexane until the organic layer is colourless. The combined isohexane extracts are washed twice with 30 ml of H_2O, and then filtered through cotton wool and evaporated under reduced pressure at 45°. The residue is dissolved in a mixture of 1·5 ml of ethyl acetate and 28·5 ml of light petroleum and slowly added to a column of alumina (see below). The flask is washed with two 5-ml portions of ethyl acetate - isohexane (1:19) and these are added to the column. The column is developed with a mixture of these solvents (1:14) until the 2:4-dinitrophenylhydrazones of cinerin I and pyrethrin I have been eluted (4·5 hr.). The cinerin II and pyrethrin II bands are then half-way down the column and are eluted with a 1:7 mixture of the same solvents (2 hr.). The collected fractions are evaporated and made up to 100 ml with isohexane. Aliquots (5 ml) are evaporated, dissolved in spectroscopically pure ethanol and made up to 100 ml, and the extinctions are measured at 377 mμ, in a 1-cm cell. The individual contents of the preparation are computed by means of a standard curve for the pyrethrin I derivative. By allowing for differences in molecular weight the four constituents may be calculated. The column consists of a tube (26 in. × 0·6 in.) containing three 6-in. portions of alumina, slurried with isohexane, and separated by 0·75 in. of isohexane and a 0·5-in. plug of cotton wool. D. C. Armsworth

5055. **Rapid combustion and determination of residues of chlorinated pesticides using a modified Schöniger method.** D. J. Lisk (New York State Coll. of Agric., Cornell Univ., Ithaca, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (2), 119–121.—Residues of chlorinated pesticides on plants are determined by evaporating a benzene extract in a cone of cellulose acetate, which is then burned in an O-filled flask, the HCl formed being absorbed in dil. NaOH soln., and the chloride measured spectrophotometrically. Complete combustion is obtained by means of a specially designed platinum holder for the folded cone, and a balloon is attached to the flask for pressure control to ensure safety. Recoveries of DDT, Thiodan (6:7:8:9:10:10-hexachloro-1:5:5a:6:9:9a-hexahydro-6:9-methanobenzo-2:4:3-dioxathiepin 3-oxide), and lindane from lucerne were 63 to 109%. M. D. Anderson

5056. **Determination of 1-naphthyl methylcarbamate (Sevin) residues in apples.** H. J. Hardon, H. Brunink and E. W. van der Pol (Keuringsdienst van Waren, Keizersgracht 732–734, Amsterdam, Netherlands). *Analyst*, 1960, **85**, 187–189.—The sample (1 kg, in pieces) is extracted overnight with dichloromethane and the residue from the evaporation of the filtered extract is heated to b.p. with methyl cyanide. The cooled filtered mixture is diluted and extracted with light petroleum, the petroleum layer being discarded. The methyl cyanide - water layer is diluted with water and extracted with dichloromethane. The residue from evaporation of the washed extract is dissolved in ethanol, water is added and the ice-cold liquid is treated with $NaNO_2$ soln. and a soln. of sulphanilamide in HCl. After 10 min., 4 *N* NaOH is added, the vol. is adjusted and the product is set aside in a refrigerator for ≮3 hr. The extinction is measured at 520 mμ and referred to a calibration graph. Recovery of known amounts was 96%. A. O. Jones

5057. **Determination of dieldrin.** E. A. Baker and E. J. Skerrett (Res. Sta., Long Ashton, Bristol, England). *Analyst*, 1960, **85**, 184–187.—The procedure described was used for the determination of dieldrin deposits on special spray-target papers and on mangold foliage. Benzene washings of the spray-target papers mixed with CaO and acetic anhydride are passed through an alumina column which is eluted with benzene. The residue from evaporation of the eluate is heated at 100° with acetic anhydride containing a specified small amount of H_2SO_4. The product is shaken with benzene and water, the separated and washed benzene layer is evaporated, and the soln. of the residue in ethanol is heated with 2:4-dinitrophenylhydrazine in H_2SO_4. The soln. of this product in benzene is washed according to a specified procedure. After addition of ethanol and a drop of tetraethylammonium hydroxide soln., the extinction is measured at 440 mμ and referred to a calibration graph. Recovery from spray-target papers was good. With deposits on mangold leaves, recoveries were reasonably good, provided that a high blank value could be tolerated. A. O. Jones

5058. **Determination of OO-dimethyl S-(N-methylcarbamoylmethyl) phosphorothiolothionate in technical Rogor and its formulations.** L. F. Dupée, K. Gardner and P. Newton (Anal. Dept., Fisons Pest Control Ltd., Cambridge, England). *Analyst*, 1960, **85**, 177–184.—The soln. of OO-dimethyl

S-(N-methylcarbamoylmethyl) phosphorothiolothionate (dimethoate) in ethyl ether is applied to a column of Hyflo Super-Cel and the column is eluted with a mixture of *iso*propyl ether and light petroleum. Fractions are collected and transferred to separate Kjeldahl flasks, water is added and the organic layer is removed by heating. The residue is evaporated to fuming with $HClO_4$ and HNO_3, cooled, diluted with water and boiled. Ammonium vanadate is added, and the extinction is measured at 470 mμ and referred to a calibration graph prepared with KH_2PO_4. From the total P content, the content of dimethoate is calculated. Alternatively, if the sample is free from interfering substances, the combined fractions of eluate containing dimethoate are extracted with water, the extract is boiled, cooled, treated with a $KBrO_3$ - KBr reagent and HCl and, after 4 min., KI is added and the liberated iodine is titrated. A vol. of blank eluate is treated similarly. A. O. JONES

5059. **The analysis of Pestox [schradan].** A. Polizu. *Rev. Chim., Bucharest*, 1960, **11** (3), 175–177.—The proposed method is based on that of Hartley (*J. Sci. Food Agric.*, 1951, **2**, 303). The biologically active octamethylpyrophosphoramide (**I**) and decamethyltriphosphoramide (**II**) are determined, but not the other components of the mixture. *Procedure*—The sample (3 to 7 g) is treated with 1 ml of 4 *N* NaOH, and diluted to 100 ml with water. A 20-ml aliquot is treated in a separating-funnel with 5 to 6 g of NaCl, and shaken until nearly all the NaCl is dissolved The esters are extracted with 4 × 20 ml of chloroform. The aq. layer is treated with an equal vol. of conc. HCl, and heated under reflux for 1·5 hr. The total amines are then determined by alkali treatment, distillation and titration of the distillate with 0·1 *N* HCl (*a*). A further 10 ml of the original soln. is heated under reflux with 5 ml of 4 *N* NaOH and 5 ml of water for 15 min. It is then cooled and treated as above, giving titration (*b*). A third portion (60 ml) of the soln. is treated with 10 ml of 4 *N* NaOH and heated under reflux for 8 hr. After cooling, the soln. is treated as for (*a*), giving titration (*c*). The components are then calculated from the formulae—

$$\mathbf{II}(\%) = 78{\cdot}6 \times 10\,[(b - a/2)]/g,$$

$$\text{and } \mathbf{I}(\%) = 71{\cdot}5 \times 10\,[c - (b + a/2)]/g,$$

where g is the amount of sample used. Errors are ±0·7% for **I** and ±2·3% for **II**. H. SHER

See also Abstract—**4657**, Water in leaves and soil.

5.—GENERAL TECHNIQUE AND APPARATUS

General

5060. **New automatic recording balance suggests possible uses besides weighing.** R. H. Müller. *Anal. Chem.*, 1960, **32** (3), 97A-98A.—The automatic electro-balance described can be used in a small confined space from −20° to +50° and from dryness to saturation. It has a rapid response and can be used with any recorder or in conjunction with a voltmeter, a digital voltmeter or electronic data-handling equipment. Its versatility suggests that it may have uses for, *e.g.*, torque measurements, etc. K. A. PROCTOR

5061. **Isolation of microbalances against vibrations.** E. Kissa (E. I. du Pont de Nemours & Co. Inc., Wilmington, Del., U.S.A.). *Microchem. J.*, 1960, **4** (1), 89–95.—Three types of balance mount were tested, and the following conclusions were reached. (*i*) Balance mounts with properly selected springs isolate the balance from disturbing vibrations with the exception of those of very low frequencies; (*ii*) a rigid mount without resilient parts neither absorbs nor magnifies vibrations; (*iii*) indiscriminate use of resilient material in the mount can result in amplification of vibrations; (*iv*) bolting the balance to the mount appears to be advantageous. G. P. COOK

5062. **Simple helium densitometer.** R. J. Kokes (Chem. Dept., John Hopkins Univ., Baltimore, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 446–447.—The densitometer described is simple in design and operation and can be used for small samples with an accuracy comparable to that reported for older methods. K. A. PROCTOR

5063. **Pipetting device for volumes of 10^{-4} to 10^{-9} millilitres.** N. Farlow, S. Wiel and J. Polissar (Naval Radiological Defense Lab., San Francisco). *U.S. Atomic Energy Comm.*, Rep. USNRDL-TR-389, Nov., 1959. 17 pp.—The instrument employs a micro-manipulator to hold and manoeuvre a fine glass capillary pipette under a wide-field stereoscopic microscope. The capillary is a replaceable unit having a male ball joint at one end which is clamped in a socket joint at the manipulator arm. Air pressure or vacuum communicated to the pipette through the bore of the ball and socket joint by a piping and valve system permits precise control of pressure on the liquid column in the capillary. By balancing capillary attraction with air pressure, a liquid column can easily be brought to rest at any point in the pipette. Scale marks placed on the exterior of the pipette can be accurately related to the liquid volume by a simple calibrating procedure, reliable to ≃2% in the 10^{-4} ml region and to ≃8% in the 10^{-9} ml zone. NUCL. SCI. ABSTR.

5064. **Rapid injection and automatic refill pipette.** H. V. Malmstadt and G. P. Hicks (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 445–446.—The pipette described operates by remote switching to deliver an aliquot of reagent rapidly in synchronisation with other operations, and also automatically refills so that it needs no attention from one aliquot to another. It is easily assembled from readily available components and has proved useful and reliable in many procedures. K. A. PROCTOR

5065. **A precision burette.** R. A. Chalmers and D. A. Thomson (Chem. Dept., Univ. of Aberdeen, Gt. Britain). *Analyst*, 1960, **85**, 226–228.—The burette described in detail has a precision of 1 in 1770 with vol. of ≃20 ml. Its main advantages are the high degree of control over the addition of reagent and the ease with which the titration can be terminated at the exact end-point. A. O. JONES

5066. **A micro-titration apparatus and its applications.** R. Berret (Centre de Rech., Roussel-Uclaf). *Bull. Soc. Chim. France*, 1960, (2), 271–275.—A titrimetric apparatus is described with which

analysis for functional groups can be carried out with samples of ≃2 mg. Titration cells of 0·5 to 10 ml capacity with platinum stirrers are used, and a platform fits over the cell carrying electrodes for any desired electrometric titration. A gas barrier to prevent carbonation of alkalis and a micro-pipette (with a precision of 0·3%) suitable for use with non-aq. solvents are described. A combined heating block and condenser for heating cells without loss of solvent is described. Various applications of the apparatus are described in detail.

E. J. H. BIRCH

5067. **Continuous gas titration analyser for fluorine.** C. W. Weber (Tech. Div., Gaseous Diffusion Plant, Union Carbide Nuclear Co., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 387–391.—An automatic apparatus is described in which the F is allowed to react in a stream of SO_2, and the reduction in molar flow of the gases is measured continuously. Since the F reacts completely with SO_2 under the given conditions, and since other gaseous components such as UF_6, O and HF do not react, the reduction in molar flow provides a direct measure of the F content. The precision of the analyser system is estimated to be ≃±1% (absolute). The principles of continuous gas titration could be applied to the analysis of other gaseous systems. J. H. WATON

5068. **A simple design of Schöniger flask.** K. Eder (École de Chimie, Univ., Geneva). *Mikrochim. Acta*, 1960, (3), 471–473 (in German).—A ground glass stopper fitting the flask is extended to form a glass loop which can carry the sample in its roll of paper. T. R. ANDREW

5069. **Fractional distillation apparatus for use in spectrographic analysis.** L. Pszonicki (Inst. Badań Jądrowych, Polsk. Akad. Nauk, Warszawa). *Chem. Anal., Warsaw*, 1960, **5** (1), 139–147.—The equipment used and the method for the preliminary fractional distillation of spectrographic samples is described. The sample is heated electrically in a graphite crucible. The vapours of the impurities are condensed directly on the electrode used for spectrographic determination. The distillation is carried out under atmospheric conditions and the temp. is recorded by means of a photocell. This preliminary fractional distillation increases the limit of detectability of many elements. M. MORAN

5070. **Centrifugal filtration apparatus.** E. L. Anderson (Organic Chem. Div., Res. and Process Development Dept., S.A. Iron and Steel Industrial Corporation Ltd., Pretoria, S. Africa). *Analyst*, 1960, **85**, 228–230.—In the apparatus described, the filter is formed by grinding a glass bulb into the mouth of a flask to give a hemispherical ground surface on the bulb. Filtration takes place through the pores of the contacting surfaces. A stainless-steel apparatus, described in detail, carries the weight of the filtering-flask, filter and funnel during the centrifuging, so that the receiving flask is free from this load. A. O. JONES

5071. **Viscosity measurement. The kinetic energy correction and a new viscometer.** M. R. Cannon, R. E. Manning and J. D. Bell (Chem. Engng Dept., Pennsylvania State Univ., University Park, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 355–358.—An improved Ubbelohde viscometer is described which has a negligible kinetic energy correction over a viscosity range of 0·4 to 20,000 centistokes. It involves a simple correlation based on the fact that the kinetic energy coeff. varies with the Reynolds number and has excellent precision for kinematic dilution and internal viscosity measurements.

K. A. PROCTOR

5072. **A simple rapid vapour pressure micro-method.** C. Y. Shen and R. A. Herrmann (Inorg. Chemicals Div., Monsanto Chemical Co., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 418–420.—The method described depends on the change of position of a mercury plug acting as a free piston in a capillary tube. The unit is inexpensive and will withstand temp. up to 400° and pressures up to 20 atm. With open-end capillaries, reproducible results within 5% of the true value are obtained, but at high temp., when sealed tubes must be used, the results are low. This error can be greatly reduced by the use of Vycor glass of low thermal expansion, and an inert gas to avoid reaction between the mercury and O. K. A. PROCTOR

See also Abstracts—**4654**, Disadvantages of polyethylene bottles for storing water. **4747**, Analysis of gases. **4807**, Micro-Dumas apparatus for determination of N.

Chromatography, ion exchange, electrophoresis

5073. **Some expedients for column chromatography.** R. P. Harpur (Inst. of Parasitology, McGill Univ., Macdonald Coll., P.O., Quebec, Canada). *Chemist Analyst*, 1960, **49** (1), 24–26.—Four electrical aids to column chromatography are described: (*i*) a mercury switch for producing a short electrical signal which operates a motor-powered turntable used for fraction collecting; (*ii*) a siphon switch needing no glass-to-metal seals and operating with one inexpensive relay; (*iii*) a siphon counter constructed from a counting device taken from a "pin ball" amusement-arcade machine; and (*iv*) a siphon counter for collecting fractions of variable vol., constructed from part of the coin-dispensing mechanism from a similar machine.

G. S. ROBERTS

5074. **Automatic fraction collector.** H. Zahnd and M. Citron (Chem. Dept., Brooklyn Coll., New York, U.S.A.). *Chemist Analyst*, 1960, **49** (1), 29.—A relatively cheap automatic fraction collector, in which is incorporated a refrigerator-defrosting timer, is described. G. S. ROBERTS

5075. **Chromatograph.** V. E. Azen and V. A. Latyshov. USSR Pat. 121,970 (18.8.59).—The chromatograph is based on standard parts, but the measuring unit consists of a condenser within which the chromatographic column is mounted. One half of the condenser is made up of several independent segments connected to an impulse generator, the impulse passing successively to each segment; the other half is the collector plate, which is connected to an amplifier and an oscillographic tube. The capacity of the condenser depends on the dielectric constant of the appropriate segment of the column, and this depends on the presence of

adsorbed material on the column. Thus the presence of adsorption zones is shown by the form of the wave on the oscillograph. C. D. KOPKIN

5076. **Apparatus for centrifugal acceleration of paper chromatography.** J. R. Tata and A. W. Hemmings (Nat. Inst. for Med. Res., Mill Hill, England). *J. Chromatography*, 1960, **3** (3), 225–229 (in English).—In the apparatus and procedure described, radially arranged strips of filter-paper are used instead of circular sheets, whilst a wad of filter-paper soaked in the solvent in the aluminium development-dish acts as solvent reservoir. Development time is reduced from several hours to a few minutes, sharper resolution is attained and there is no distortion of patterns, either in adsorption or partition chromatography. The method is specially adapted to the quant. analysis of substances labelled with radio-isotopes having short half-lives. For example, in the chromatographic analysis of ^{82}Br-labelled halogenated tyrosines, thyronines and their deriv. with the solvent system *n*-butanol - acetic acid - H_2O (39:5:6, by vol.), the time taken for chromatogram development and radioactivity recording of 24 strips is $\simeq$8·5 hr. in comparison with $\simeq$40 hr. for conventional ascending chromatography. W. J. BAKER

5077. **Zone migration in paper chromatography.** J. C. Giddings, G. H. Stewart and A. L. Ruoff (Dept. of Chem., Utah Univ., Salt Lake City, U.S.A.). *J. Chromatography*, 1960, **3** (3), 239–251 (in English).—An extensive theoretical and experimental study of the influence of concn. gradients on zone migration is reported, and precautions that must be taken in interpreting data in paper chromatography are indicated. The equation $R_F = A_M/(\alpha A_S + A_M)$ (where A_M is the cross-sectional area of mobile phase normal to direction of flow, and A_S is the cross-sectional area of stationary phase) does not correctly relate R_F to the partition coeff. α. The R_F value shows an initial transient period during which it approaches a limiting value. The limiting and transient values are calculated for the migration of methyl orange on Whatman 3 MM paper with a H_2O-saturated *n*-butanol solvent. Radial flow with variable-length wicks is also discussed and, by using the data from rectangular flow, values of R_R for the same methyl orange system are calculated; these values agree with the experimental ones. The zone-migration curves do not always follow the order R_F, R_R and R_R^3; the reasons for deviation from the relation $R_R^3 = R_F$ are discussed. W. J. BAKER

5078. **Multiple zones and spots in chromatography.** R. A. Keller and J. C. Giddings (Dept. of Chem., State Univ., Tucson, U.S.A.). *J. Chromatography*, 1960, **3** (3), 205–220 (in English).—By reference to examples, various theories to explain double or multiple spotting in the paper chromatography of single pure substances are discussed and correlated. Theoretical equations for calculating spot shapes and concn. profiles are derived kinetically for multiple spots caused by the slow interconversion of chemical species undergoing electrophoretic migration. Some instances of typical spot profiles are shown, and methods for determining the true origin of multiple spotting are discussed. Multizoning can lead to erroneous conclusions in mixed chromatograms where an unknown and a known compound are mixed and chromatographed. (35 references.) W. J. BAKER

5079. **An eluter for paper chromatograms.** M. Saffran and D. F. Sharman (Pharmacology Dept., Univ. Edinburgh, Scotland). *Canad. J. Biochem. Physiol.*, 1960, **38** (3), 303–305.—The eluter (illustrated) consists of a tube with a female ground-glass joint at the top and a male joint at the bottom. Sealed into the tube is a cylindrical well to contain the eluting solvent. A specially-shaped filter-paper wick is inserted into the well and the paper to be eluted is rolled into a cylinder and placed in the tube in contact with the wick. The well is filled with solvent, the eluter is stoppered, and a test-tube is fitted to the bottom. R. A. BRENAN

5080. **Elution apparatus for paper chromatography.** J. Skolik (Inst. for Plant Breeding, Polish Acad. Sci., Poznań, Poland). *J. Chromatography*, 1960, **3** (3), 273–275 (in German).—The construction and operation are described of an arrangement, of flexible dimensions, whereby almost any number of filter-paper strips can be rapidly eluted and the elution period controlled to a large extent (by changing the width and type of paper). The results obtained in the chromatographic micro-determination of lupin alkaloids by the bromothymol blue method are reported. Self-absorption by the paper is minimised, being generally $<3\%$. W. J. BAKER

5081. **Simple fluorescent intensification screen for ultra-violet scanner cameras.** D. F. Petersen and A. Murray, III (Los Alamos Sci. Lab., Univ. of California, Los Alamos, N. Mex., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 443.—Filter-paper can be impregnated with ethanolic soln. of 1-methyl-4-(5-phenyl-2-oxazolyl)pyridinium toluene-*p*-sulphonate to obtain homogeneous backgrounds of light blue or yellow fluorescence against which areas of a paper chromatogram containing u.v.-absorbing substances appear as distinct dark shadows. Such screens are simple to prepare, are very stable and give sharper outlines than those obtained with coated glass screens. K. A. PROCTOR

5082. **Preservation of paper chromatograms sprayed with ninhydrin.** A. J. Woiwod (Wellcome Res. Lab., Beckenham, Kent, England). *J Chromatography*, 1960, **3** (3), 278 (in English).—High stability of colour and intensity is assured if chromatograms of amino acids that have been sprayed with ninhydrin at 80° are immediately sealed in a polyethylene bag and stored in the dark at $\simeq$4°. The original colour differentiation is retained for $>$14 days and the subsequent purple colours do not change much during 3 months' storage. The preferred spray is prepared by dissolving ninhydrin (200 mg) in collidine (0·2 ml) and making the soln. up to 100 ml with $CHCl_3$. W. J. BAKER

5083. **Automatic direct quantitation of radioactivity on paper chromatograms.** H. Ludwig, V. R. Potter, C. Heidelberger and C. H. de Verdier (Wisconsin Univ. Med. Sch., Madison, U.S.A.). *Biochim. Biophys. Acta*, 1960, **37** (3), 525–527.—The assembly and circuit modifications of commercial (U.S.) components for the automatic recording of radioactivity in spots on paper chromatograms are described. The apparatus is satisfactory for wide

variations in activity, and records the rate of counting and the total counts in each peak, regardless of counting rate, on a number of strips taped together to a total length of 50 ft. Operation is automatic for periods up to 2 days.

W. H. C. SHAW

5084. **Salting-out chromatography. VI. Effect of length of the hydrocarbon chain, the eluent salt, and the cross-linking and ionic form of the resin.** A. Breyer and W. Rieman, III (Ralph G. Wright Chem. Lab., Rutgers, N.J., U.S.A.). *Talanta*, 1960, **4** (1), 67–74.—In the homologous series acetone, butanone, and pentan-2-one, each additional CH_2 causes a nearly constant rise in the log of the distribution ratio. Increased cross-linking in sulphonated polystyrene (Dowex 50) decreases, but in quaternary N-bearing polystyrene (Dowex 1) increases, the distribution ratio. The highest distribution ratio is obtained when the counter ion of the resin has the least salting-out effect. J. P. STERN

5085. **Informal gas-chromatography symposium.** W. W. Brandt (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 339–340.—A report of a discussion at the Amer. Chem. Soc. meeting at Atlantic City is presented. The topics discussed were capillary columns and the significance of numbers of theoretical plates in relation to performance, the relative merits of different types of detector, especially ionisation detectors, and high-temp. chromatography. G. BURGER

5086. **Gas - liquid chromathermography.** A. G. Nerheim [Res. and Devel. Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1960, **32** (3), 436–437.—Chromathermography has been modified by moving the heater down the column more than once in order to improve the resolution and compress the bands. For the first pass, the temp. of the gradient is less than the characteristic temp. of the higher-boiling components, so that only the lower-boiling components are eluted. Subsequent passes down the column at successively higher temp. causes the higher-boiling components to be eluted as separate bands.

K. A. PROCTOR

5087. **Theoretical plates in gas chromatography. Effects of distribution ratio, viscosity, and amount of liquid phase.** J. J. Duffield and L. B. Rogers (Dept. of Chem., Mass. Inst. Technol., Cambridge, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 340–343.—The importance of the three variables, distribution ratio, film thickness, and diffusion, in the "mass-transfer" term (C) in the equation of van Deemter *et al.* (*Chem. Eng. Sci.*, 1956, **5**, 271) has been studied. If one or two of these variables are adjusted so as to minimise the value of C, then the effect of the remaining variables appears to be nearly non-existent. K. A. PROCTOR

5088. **Separation factors in gas chromatography.** W. A. Wiseman (Gas Chromatography Ltd., 176 Old Brompton Road, London, S.W.5, England). *Nature*, 1960, **185**, 841–842.—The separation of *m*- and *p*-xylene can be achieved on a 50-ft. capillary column, coated with dinonyl phthalate, with Ar (1 ml per min.) as the carrier gas, at room temp., the separation factor being 1·05. Although the plate number remains the same, no separation is achieved at 80°, because the principal separation factor is the difference in the vapour pressures of the two xylenes, which is much less at elevated temp. than at room temp. K. A. PROCTOR

5089. **Retention temperature and column efficiency in programmed-temperature gas chromatography.** H. W. Habgood and W. E. Harris (Research Council of Alberta, Edmonton, Canada). *Anal. Chem.*, 1960, **32** (4), 450–453.—It is recommended that results of programmed-temp. gas chromatography should include both r/F values (where r is dT/dt and F is flow rate) and retention temp. of the peaks. It is possible to predict from isothermal measurements the relationship between r/F and retention temp., and this has been confirmed experimentally. For any given column the retention temp. depends on the ratio of heating rate to carrier-gas flow rate rather than on either alone. In the work described, a flow of about 40 to 50 ml per min. and a heating rate of 4° to 5° per min. are indicated as giving the most efficient column operation. K. A. PROCTOR

5090. **Heater for gas-chromatographic columns.** J. N. Roper, jun. (Res. Lab., Tennessee Eastman Co., Kingsport, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 447–448.—A compact, easily constructed furnace is described using the radiant heating principle with bare wire heating elements and polished walls to confine and reflect the heat towards the coiled column. As no insulation is needed the furnace can be easily opened on hinges for rapid cooling and ready access to the column for replacement or repacking. The temp. stability is good (no change $>1°$ per hr. has been observed) and the heating rate is rapid enough to allow the programmed temp.-rise technique to be used. K. A. PROCTOR

5091. **Sucrose acetate *iso*butyrate as a new ester liquid phase for gas - liquid partition chromatography.** D. M. Smith, J. C. Bartlet and L. Levi (Food and Drug Directorate, Tunney's Pasture, Ottawa, Canada). *Anal. Chem.*, 1960, **32** (4), 568–569.—Sucrose diacetate hexa*iso*butyrate is recommended as a strongly polar ester stationary phase which does not have the non-uniformity and thermal instability exhibited by other materials. It decomposes above 200°, but the only volatile decomposition products are acetic and *iso*butyric acids, which do not char in detector systems of the hot-wire type. K. A. PROCTOR

5092. **Molecular sieves as subtractors in gas-chromatographic analysis. II. Selective adsorptivity with respect to different homologous series.** N. Brenner, E. Cieplinski, L. S. Ettre and V. J. Coates (Perkin-Elmer Corp., Norwalk, Conn., U.S.A.). *J. Chromatography*, 1960, **3** (3), 230–234 (in English).—The use of Linde mol. sieves (4A, 5A, 13X) for the irreversible adsorption of specific components is discussed by reference to the behaviour of homologous series (normal, iso- and cycloparaffins, esters, ketones, normal and iso-alcohols) and of such materials as CO, O, N, CS_2, methane, nitromethane, inert gases and thiophen on a 50-cm column at 100° with He as carrier gas. It is possible to select a mol. sieve that will retain the required component in a sample while the others pass through the column. Components that pass through

with virtually no retention time can be separated by inserting a standard partition column in series with the sieve(s). Removal of an adsorbable component by a short column of mol. sieve will permit subsequent observation and measurement of peaks otherwise obscured by overlap, *e.g.*, of acetone by propionaldehyde in a mixture of these with *iso*propyl ether, ethyl acetate and ethanol. For subtractive purposes, mol. sieves should be used at high temp. (100° to 130°) to minimise retention times of components that are not irreversibly held.

III. Secondary effect of the molecular-sieve trap column. L. S. Ettre and N. Brenner. *Ibid.*, 1960, **3** (3), 235–238.—When using mol. sieve 5A as a trap for the specific adsorption of a component, *e.g.*, propionaldehyde, from mixtures of organic compounds containing CO or OH groups, there is a secondary reaction whereby the component, *e.g.*, acetone, that should leave the column is retained under the influence of the adsorbed component. The effect is confined to concn. of acetone $<5\%$ in propionaldehyde and to concn. of *iso*propyl ether $<0{\cdot}5\%$ in water. Hydrocarbons show no such secondary adsorption effect. W. J. BAKER

5093. **Response of thermal-conductivity cells in gas chromatography.** L. J. Schmauch and R. A. Dinerstein [Res. and Devel. Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1960, **32** (3), 343–352.—Studies have been made of the response of cells to changes in gas composition and operating temp. An equation has been derived in which the response is considered as the product of two factors: a cell factor, which depends on operating conditions, and a thermal-conductivity factor which is related to the difference in the conductivities of the carrier gas and of the gas mixture passing through the cell when a component is eluted. K. A. PROCTOR

5094. **Integrating counter cell for use with vapour-phase chromatography.** G. Blyholder (Dept. of Chem., Johns Hopkins Univ., Baltimore, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 572.—The cell described has been designed so that the integrated activity of a slug of gas can be measured regardless of the spread of the slug, and in this way many calibration difficulties are avoided.

K. A. PROCTOR

5095. **Catalytic combustion as a detection method in gas chromatography.** J. Sládeček (Inst. Chem. Technology, Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (3), 636–641 (in German).—The catalytic combustion of components on heated platinum wire increases the sensitivity of detection in gas chromatography. A description of the suggested apparatus is given with a discussion and critical evaluation of advantages and disadvantages of the method.

J. ZÝKA

5096. **Analogue integrator for gas-chromatography apparatus.** Z. Böhm (Inst. f. Erdölforschung, Brno, Czechoslovakia). *J. Chromatography*, 1960, **3** (3), 265–272 (in German).—With the arrangement described and illustrated the area below the curve of the output voltage of the indicator in a gas-chromatography unit can be measured directly, and the value (equiv. to component concn.) recorded in print. The device is at present a separate part, but will eventually be combined with the automatic gas chromatograph so that the calculated values are printed at the corresponding curves.

W. J. BAKER

5097. **Design and use of a refined micro-electrophoresis unit.** B. W. Grunbaum and P. L. Kirk (Dept. of Pathol., Univ. of Calif., Sch. of Med., San Francisco, U.S.A.). *Anal. Chem.*, 1960, **32** (4), 564–566.—The apparatus described enables eight 0·01 to 0·1-μl samples to be run simultaneously on precision-cut multistrip papers. The results show a high reproducibility. H. F. W. KIRKPATRICK

See also Abstract—**4825**, Flash exchange gas chromatography.

Optical

5098. **Spectrograph with photo-electric recording of the optical spectrum.** G. A. Izmallov. USSR Pat. 121,264 (15.7.59).—The spectrograph has a charged photo-conducting plate on an electrically conducting support at the focal plane to record the spectrum. The plate is discharged proportionally to the amount of light falling on it. The transcribing of the electrostatic image to an oscillographic record is described. C. D. KOPKIN

5099. **Spectral analysis of solutions using two rotating electrodes.** W. Guttmann, H. Becker and G. Müller-Uri (Dtsch. Akad. Wissenschaften, Inst. f. Ernährung, Potsdam-Rehbrücke). *Naturwissenschaften*, 1960, **47** (6), 128–129 (in German).—The soln. to be tested is atomised in a chamber and the aerosol is passed through the gap between two electrodes, set at an obtuse angle, both of which are caused to rotate in opposite directions about their longitudinal axes. The discharge thus takes place in a fixed position in a horizontal plane. Improved sensitivity and reproducibility over the simple rotating electrode system are claimed. H. M.

5100. **Spectrochemical analysis of solutions by the spraying technique.** I. A. Voinovitch (Soc. Franç. Céram. Centre. Nat. d'Études et de Rech., Paris, France). *Chem. Anal., Warsaw*, 1960, **5** (1), 85–93.—Solutions are injected as aerosols into the arc. The influence of sprays and burners on the accuracy and sensitivity of the method were investigated. In determinations of Al_2O_3 and SiO_2 in clay the accuracy of the results depended upon the type of the spray and regularity of the evolution of gas employed for spraying. Attempts to combine flame photometry with a spectrographic technique by combining the acetylene - oxygen burner with a d.c. arc failed to produce conclusive results.

W. B. MIASKOWSKI

5101. **Design and use of an improved rotating disc electrode for spectrographic analysis of solutions.** H. J. Philcox (East Malling Res. Sta., Kent, England). *Spectrochim. Acta*, 1960, **16** (3), 384–389.—The construction of an apparatus in which the conventional carbon disc is replaced by a disc of filter-paper sandwiched between copper discs is described in detail. Application to the determination of Ca (0·6 to 4·5%), Mg (0·1 to 0·8%), Mn (15 to 300 p.p.m.), B (20 to 130 p.p.m.) and Fe (50 to 500 p.p.m.) in acid soln. of plant ash is described.

The coeff. of variation is ≃3 to 4% for all elements, and reasonable agreement with chemical determinations is shown. P. T. BEALE

5102. **Simple atomic absorption spectrophotometer.** G. F. Box and A. Walsh (Div. of Chem. Phys., C.S.I.R.O., Chem. Res. Labs., Melbourne, Australia). *Spectrochim. Acta*, 1960, **16** (3), 255–258.—Modulated radiation from a hollow-cathode light source passes through a flame into which the solution to be analysed is sprayed. The appropriate resonance line from the light source is selected by means of a monochromator, and its absorption by the flame is measured by a photomultiplier tube, the modulated output of which is fed to an a.c. amplifier, a rectifier and a d.c. milliammeter. The electrical circuits and suitable components are described. The apparatus is capable of absorption measurements to within ±0·25% and can be used for emission flame photometry by placing a chopper between the flame and the entrance slit of the monochromator. P. T. BEALE

5103. **The role of some organic solvents in flame photometry.** R. Avni and C. T. J. Alkemade (State Univ., Utrecht, Netherlands). *Mikrochim. Acta*, 1960, (3), 460–471 (in English).—The effect of various concn. of acetone, methanol and *n*-propanol on the Na emission and flame temp. has been investigated at various air - acetylene ratios and flame heights. T. R. ANDREW

5104. **Recording spectrofluorimeters: two new designs and their evaluation.** J. W. Goldzieher, W. S. Bauld, L. L. Engel and M. L. Givner (Dept. of Endocrinology, Southwest Foundation for Res. and Education, San Antonio, Tex., U.S.A.). *Canad. J. Biochem. Physiol.*, 1960, **38** (3), 233–243.—The construction of two new spectrofluorimeters is described. Most of the components are commercially available and the remainder are readily made. The performance of the two instruments is compared with that of the commercially available Aminco - Bowman model, and the advantages and disadvantages of the three instruments are tabulated. R. A. BRENAN

5105. **Methods for obtaining correction factors for fluorescence spectra as determined with the Aminco - Bowman spectrophotofluorimeter.** C. E. White, M. Ho and E. Q. Weimer (Dept. of Chem., Univ. of Maryland, College Park, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 438–440.—Methods are described for correcting excitation spectra for the variation in the intensity of the exciting radiation at different wavelengths and emission spectra for the response characteristics of the phototubes and the grating. K. A. PROCTOR

5106. **Automatic recording of derivative ultraviolet spectra. Application in steroid structure determination.** E. C. Olson and C. D. Alway (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 370–373.—A simple inexpensive attachment for the Cary Model 11 recording spectrophotometer is described that permits direct recording of the first derivative of an u.v. spectrum. The technique has been used to distinguish between 6α- and 6β-methyltestosterone and between 6α- and 6β-methylprogesterone and for the location of substituents. A. R. ROGERS

5107. **Precision temperature control of spectrophotometer cells. A comparison of water circulation and electrical systems for the Unicam SP. 500.** N. Macleod (Univ., Leicester, England). *Chem. & Ind.*, 1960, (13), 342–344.—The temp. control of the water-circulating unit described is limited by the design of the water-flow passages; the water-circulation rate is inadequate for maintaining a reasonably constant temp. under ordinary ambient temp. changes. Electronically controlled electrical heating, however, can maintain the cell temp. at 50° with a variation of ≯ ±0·02°; the apparatus is also more compact. G. P. COOK

5108. **Infra-red spectrograph.** L. V. Belyakov, I. A. Voltsekhovskaya and G. I. Rekalova. USSR Pat. 125,920 (1.2.60).—The radiation receiver is a single crystal of indium antimonide in the field of a permanent magnet; the resulting photomagnetic alternating e.m.f. is amplified, rectified, and measured on a potentiometer or displayed on an oscillograph. C. D. KOPKIN

5109. **Infra-red cells for volatile and pyrophoric materials.** D. M. Robins, J. P. Faust and W. W. Harple (Energy Div., Olin Mathieson Chemical Co., Niagara Falls, New York, U.S.A.). *Chemist Analyst*, 1960, **49** (1), 28.—A simple i.r. cell, constructed from a length of glass tubing with vacuum attachments fused into the walls, suitable for direct sampling of volatile and pyrophoric materials, is described. G. S. ROBERTS

5110. **Investigation of small quantities of substances with the Zeiss infra-red spectrophotometer.** E. Steger (Inst. Inorg. and Org. Tech. Chemistry, Tech. High School, Dresden). *Chem. Tech., Berlin*, 1960, **12** (4), 216–219.—Test analyses are made of μg quantities of substances by means of the Zeiss recording i.r. spectrophotometer U.R. 10, an instrument that requires no additional optical condensers, etc., and thereby obviates incidental heat damage to the sample and incidental errors. Improved results were obtained with a few μg of the compounds. H. L. WHITEHEAD

5111. **Rotation-dispersion measurements with a normal spectrophotometer.** I. P. Dirkx, P. J. van der Haak and F. L. J. Sixma (Lab. Org. Chem., Univ. of Amsterdam, Netherlands). *Chem. Weekbl.*, 1960, **56** (10), 151–154.—A Zeiss spectrophotometer type PMQ is adapted. The slide on which the cells are placed in normal absorbance measurements is replaced by a slide on which, in addition to the cells, four polarisation prisms are mounted. The choice of the angle between the analysing and the polarising prisms is governed by the attainable sensitivity and the expected signal-to-noise ratio. A formula for the maximum sensitivity as a function of the rotation angle is given. Under the most favourable conditions the rotation can be determined with a standard deviation of 0·004°. M. J. MAURICE

5112. **Evaluation of standard model D Keston polarimeter attachment for the Beckman DU spectrophotometer.** K. G. Poulsen (Dept. of Chem., Univ. of California, Los Angeles, U.S.A.). *Anal. Chem.*, 1960, **32** (3), 410–413.—The attachment was tested to assess its value for measuring optical rotatory dispersion, particularly in the vicinity of

an optically active absorption band. The optical rotation of aq. sucrose soln. at 20° can be determined to an accuracy of ≃2% over the approx. range 0·3° to 2° and 480 to 590 mμ. Outside these limits the error increases rapidly. A complete set of equations relating optical rotation to relative transmittance or absorbance has been derived for specified conditions.
K. A. PROCTOR

5113. **Continuous analysis by refractive-index measurement.** G. V. Jeffreys (Dept. of Chem. Engng, Birmingham Univ.). *Ind. Chem.*, 1960, **36**, 127–128, 133.—A continuous-flow type of refractometer capable of detecting a change in refractive index of 0·0003 over the entire range is described; composition changes of ≃0·3% can be measured for most binary and ternary mixtures. Results for mixtures of ethanol and benzene are compared with those obtained by density, conductivity, dielectric constant and u.v. spectrometric measurements.
S.C.I. ABSTR.

See also Abstract—**4660**, Interference of alkali metals in flame photometry.

Thermal

5114. **Improved melting-point block.** L. A. Jones and C. K. Hancock (Dept. of Chem., A. and M. Coll. of Texas, College Station, U.S.A.). *Chemist Analyst*, 1960, **49** (1), 28–29.—The construction of an aluminium block, requiring rather elaborate machining, is described. G. S. ROBERTS

5115. **Apparatus for observing physical changes at elevated temperatures. Application to differential thermal analysis.** V. D. Hogan and S. Gordon (Pyrotechnics Chemical Res. Lab., Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (4), 573–574.—The convenient and inexpensive experimental arrangement described was developed to allow visual observations to be made during differential thermal analyses. It cannot be used at temp. above 650° and only major colour changes can be distinguished at above 500° because of a strong red glow diffused by the reflector of the electric Bunsen burner which is used. K. A. PROCTOR

5116. **Sensitive thermal-conductivity gas analyser.** J. R. Purcell and R. N. Keeler (Cryogenic Engng Lab., Nat. Bureau of Standards, Boulder, Canada). *Rev. Sci. Instrum.*, 1960, **31** (3), 304–306.—Electronic circuits are described that enable a.c. potentials to be used for excitation of thermal-conductivity cells. A reduced drift and increased sensitivity as compared with d.c. excitation are claimed.
G. SKIRROW

5117. **Automatic rapid combustion apparatus for elementary analysis.** F. Vojtěch (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (3), 135–139.—The universal electric apparatus (described and illustrated) for micro- and semi-micro analysis is suitable for the micro-determination of C and H by the classical Pregl method or by new rapid methods based on the use of active combustion catalysts with external absorption of nitrogen oxides. The apparatus can be used also for the determination of halogens and sulphur by methods based on the mineralisation of organic compounds by combustion in a stream of O and for the gas-volumetric determination of N by the Dumas - Pregl method, the Zimmermann method and methods based on combustion on cobalt oxides. Automatic combustion of the compounds is carried out by means of a movable furnace. The apparatus can be used for any type of organic compound, even for explosives such as picrates, and the combustion can be completed within 5 to 6 min. J. ZÝKA

5118. **Further development of an apparatus for the more rapid and accurate analysis of gases in metals with practical results.** H. Feichtinger, H. Bächtold and W. Schuhknecht. *Schweiz. Arch. angew. Wiss.*, 1959, **25** (12), 426–439.—Vacuum-fusion equipment with a graphite crucible forms the basis of the apparatus. Gas evolution is monitored continuously and the record can be plotted against time or temp. The collected gases are then passed to a micro gas-analysis unit; for some experiments this was replaced by a high-sensitivity recording gas chromatograph. The speed of the analysis is five to ten times faster than with conventional vacuum-fusion equipment and involves fewer errors. Examples quoted refer mostly to steels, but curves are given for the gas evolution from molten copper and aluminium, from NbN decomposed *in vacuo*, and from SAP. METALLURG. ABSTR.

5119. **Venturi jet (atomiser)-type burner for determining sulphur in light petroleum products.** C. W. Brown (Socony-Mobil Oil Co., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 442–443.—Diagrams of the burner and auxiliary equipment are given. A stream of heated air draws the sample from a weighed flask through a jet and the mixture burns with a blue flame. The combustion products are absorbed in H_2O_2 soln. Regulation is by means of a stopcock in the jet tube, by control of the air flow and by adjustment of the electrical pre-heater. The rate of burning is 60 g of sample per hr. If the approx. concn. of S is unknown an electrode system is fitted into the absorber to measure the conductance and indicate when sufficient sample has been burned. The procedure for determining the correct operating conditions for a given sample is described.
G. BURGER

Electrical

5120. **A method for the micro-analysis of gas** M. Lefort (Serv. de Radiochim., Lab. de Phys. Nucl., Fac. de Sci. de Paris, Orsay, France). *Bull. Soc. Chim. France*, 1960, (2), 239–242.—An apparatus is described by which small quantities of gaseous mixtures may be analysed by means of an ionisation chamber. The chamber consists of a Kovar cylinder in the centre of which is mounted a fine copper needle as cathode; a source of 240 μC (Po) is mounted at one end. The cylinder is sealed into a tube with a ground glass joint which can be connected to the apparatus in which the gases are separated. The ionisation current is proportional to the pressure of the gas between 0·05 and 0·7 torr and the slopes increase with atomic wt. but N and O cannot be resolved. The gases at low pressure are passed through a glass circuit by a small mercury diffusion pump. Water vapour can be condensed in an acetone - solid CO_2 trap, and CO_2, N_2O, etc., with liquid N. Hydrogen is removed from the other gases by a small palladium tube heated at 200° in a furnace and O reacts with H in a similar

tube at 350° to 400° to separate it from N. The precision is 1 to 2% for 20 to 500 μl of mixed gases and 5 to 10% for 5 to 20 μl. E. J. H. BIRCH

5121. **Direct oscilloscopic evaluation of electropherograms with simultaneous integration.** J. Macků and Z. Stránský (Fac. of Med., Charles' Univ., Hradec Králové, Czechoslovakia). *Chem. Listy*, 1960, **54** (2), 145–147.—A simple method is described which renders it possible to show on the oscilloscope screen the plots of the colour density, i, of the electropherogram, and the integral of this function, $\int i dt$ against t, which vary according to the concentrations of the individual coloured fractions of the separated mixtures. A procedure is also given for obtaining the plot of the integral $\int i dt$ against i, which is more satisfactory than existing procedures. The method is tested with human serum.

J. ZÝKA

5122. **The use of the potentiostat in analytical practice.** F. Plesnivý (Res. Inst. Vacuum Electronics, Prague). *Sklář a Keram.*, 1960, **10** (4), 107–108.—The apparatus was used for the determination of Cd, Ni and Zn in electrolytic copper and of Pb and Sn in alloys. With electrolytic copper, Cu is separated from Cd, Ni and Zn by electrolysis at a constant potential, the soln. is evaporated and the waves of Cd, Ni and Zn are recorded polarographically in an aq. NH_3 - NH_4Cl buffer soln. With alloys, Pb is separated from a tartrate medium (pH 5) at a potential of 550 mV *vs.* the S.C.E., the Sn^{IV} - tartrate complex is decomposed by treatment with conc. HCl, and Sn is electrolytically separated at 650 mV from a soln. containing hydrazine hydrochloride as depolariser. J. ZÝKA

5123. **Three-component polarographic cell.** D. K. Roe and C. J. Nyman (Washington State Univ., Pullman, U.S.A.). *Chemist Analyst*, 1960, **49** (1), 27.—The versatile polarographic cell described consists of a reference-electrode compartment, a removable salt bridge and an indicator-electrode compartment. Advantages of the design include less chance of contamination of the cells because of the removable bridge, and flexibility in operation of the reference-electrode cell, achieved by fitting it with standard taper joints. G. S. ROBERTS

5124. **Development and study of a mercury cathode having a constant and renewable surface.** M.-P. Simmonin. *J. Chim. Phys.*, 1960, **57** (3), 161–201.—In the cell described and illustrated the cathode is formed by a surface of purified mercury in a tube (≃1 mm internal diam.) which is periodically renewed at intervals of 0·4 to 1 sec. by drops of mercury from another capillary (0·08 mm internal diam.) placed directly above it in the electrolyte. The mean polarisation is thus constant, there is no interference by diffusion, and the wave-height is proportional to the concn. of reducible ion whatever its nature or valency. Experimental curves of voltage *vs.* current are reported and discussed, and the equation for the discharge wave is established. The advantages claimed over the dropping-mercury electrode are that the sensitivity can be modified by varying the frequency of surface-renewal (of which $E_{\frac{1}{4}}$ is a linear function) and that no additive is necessary, since the curves of voltage *vs.* current show no maxima. The disadvantages are the high resistance, the limited range of operating potential (>2 V), and the care needed in manipulation. The electrode is suitable for the study of ion-discharge and the capacity of the double layer. (44 references.) W. J. BAKER

See also Abstract—**4769**, Amperometric determination of F^-.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	A	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	mμg
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	α_λ^t
coefficient	coeff.	ounce	oz
Colour Index	C.I.	parts per million	p.p.m.
concentrated	conc.	per cent.	%
concentration	concn.	per cent. (vol. in vol.)	% (v/v)
constant	const.	per cent. (wt. in vol.)	% (w/v)
crystalline / crystallised	cryst.	per cent. (wt. in wt.)	% (w/w)
cubic	cu.	potential difference	p.d.
current density	c.d.	precipitate (as a noun)	ppt.
cycles per second	c/s	precipitated	pptd.
density	ρ	precipitating	pptg.
density, relative	d or wt. per ml	precipitation	pptn.
dilute	dil.	preparation	prep.
direct current	d.c.	qualitative, -ly	qual.
distilled	dist.	quantitative, -ly	quant.
ethylenediaminetetra-acetic acid	EDTA	recrystallised	recryst.
		refractive index	n_λ^t
electromotive force	e.m.f.	relative band speed	R_F
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	$E_{\frac{1}{2}}$	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	$[\alpha]_\lambda^t$
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μg (not γ)	volt	V
microlitre	μl	volume	vol.
micromole	μmole	watt	W
micron	μ	wavelength	λ
milliampere	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

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